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Mathematics. — "*Determination of the Bilinear System of ∞^3 Line Elements of Space*". By Dr. G. SCHAAKE. (Communicated by Prof. HENDRIK DE VRIES).

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§ 1. A system S_3 of ∞^3 line elements (P, l) of space each consisting of a straight line l and a point P on it, has three characteristic numbers φ , ψ and χ . φ is the order of the complex of the lines l of S_3 , ψ the number of line elements of S_3 for which P lies in a definite point and χ the order of the curve of the points P of the line elements of S_3 the lines l of which lie in a given plane.

For a *bilinear* system S_3 the numbers φ and ψ are both *one*. In this case the lines l of S_3 form a linear complex C . Any plane α contains, therefore, a plane pencil (A, α) of lines l of S_3 , which has the point A of α as vertex. Also the straight line l for which P lies in A , belongs to this plane pencil, which contains at the same time all the straight lines of S_3 through A . If l describes the plane pencil (A, α) , P describes a curve which has one point outside A in common with each generatrix of (A, α) but which passes at the same time through A and touches there the line l corresponding to A ; hence this curve is a conic k^2 through A . The third characteristic number of S_3 is consequently *two*.

On the supposition that a system $S_3(1, 1, 2)$ exists, we shall now derive its properties, and then indicate how by the aid of the found properties any such a system may be constructed.

§ 2. If P moves on an arbitrary straight line r , the line l describes a scroll of which r is a single directrix. As the line elements of S_3 in a plane through r have a conic of points P , there lie in this plane two elements of S_3 of which the points P belong to r , and such a plane contains besides r two generatrices of the scroll corresponding to r , which is, therefore, of the third order. This surface σ^3 has the straight line r' associated to r relative to C , as a double directrix.

To a straight line of points P there corresponds in S_3 a cubic surface of straight lines l .

The line elements of S_1 the points of which lie in a plane V , have a congruence Φ of lines l . As the elements of S_1 of which the lines l pass through a given point, have a conic of points P , there are two among these line elements that have their points P in V , and the order of Φ is *two*. For the class of Φ the same number is found.

To a plane of points P there corresponds accordingly in S_1 a congruence (2, 2) of straight lines l .

The common lines of two congruences Φ_1 and Φ_2 of straight lines l corresponding resp. to the planes V_1 and V_2 , form a scroll (Φ_1, Φ_2) of the eighth order. For the lines of Φ_1 and Φ_2 cutting an arbitrary straight line r , form resp. two surfaces of the fourth order φ_1^4 and φ_2^4 for which the lines r and r' are double directrices and which have eight generatrices in common, as r and r' count each four times in the intersection. (Φ_1, Φ_2) consists of the scroll φ^3 associated to the straight line (V_1, V_2) , and of a scroll of the fifth order φ^5 consisting of singular straight lines of S_1 , as two different points P , hence an infinite number of points P , correspond to a generatrix l of φ^5 .

The singular straight lines l of S_1 form a scroll of the fifth order φ^5 . Each of these straight lines, together with any of its points, gives a line element of S_1 .

As an arbitrary plane has a point in common with each singular straight line, all congruences Φ pass through φ^5 .

To the five points P in which an arbitrary straight line r cuts the surface φ^5 , there correspond as straight lines l the five generatrices of φ^5 through these points. Hence:

Each surface φ^5 has five generatrices in common with φ^5 .

We can also arrive at this conclusion in the following way. An arbitrary scroll of the third order φ^3 consisting of straight lines of C , has six straight lines in common with a congruence Φ . For the straight line r splits off twice and the line r' four times from the intersection of φ^3 with the surface φ^4 consisting of all straight lines of Φ that cut the directrices r and r' of φ^3 . The points P associated to an arbitrary scroll φ^3 consisting of straight lines of C , form therefore a curve of the sixth order. Accordingly a surface φ^3 associated to a straight line r , must contain five singular lines of S_1 .

In the same way the fact that an arbitrary congruence (2, 2) of straight lines of C has six lines in common with a φ^5 , causes each congruence Φ to pass through φ^5 .

§ 3. The rays l of C which cut two arbitrary lines r_1 and r_2 ,

form a scroll λ^3 . To this scroll there corresponds a curve of points P which cuts each generatrix of λ^3 once, namely in the point associated to it. The three lines l of the surface ϱ_1^3 corresponding to r_1 which cut r_1 , are the generatrices of λ^3 the points P of which lie on r_1 . The curve associated to λ^3 has, therefore, four points in common with an arbitrary plane through r_1 .

To a scroll of straight lines l of C there corresponds in S_1 a rational curve of the fourth order k^4 of points P .

To the straight lines l which cut an arbitrary line r and which form accordingly a bilinear congruence with directrices r and r' , the points P of a surface are associated. This surface passes through r , because each point of r is the point P of a line l , and also through r' , because the line l corresponding to a point of r' , always cuts r . Besides this surface cuts each line l resting on r , hence also on r' , outside r and r' in the points P associated to l , so that it is of the third order.

To a bilinear congruence of C there corresponds accordingly a cubic surface Ω^3 .

To the scroll which two bilinear congruences of C have in common, a k^4 is associated lying on both the surfaces Ω^3 corresponding to the congruences mentioned. These surfaces have one more curve k^5 in common, consisting of points that are singular for S_1 . The lines l corresponding to a point of k^5 , form the plane pencil of straight lines of C passing through this point.

There is a quintic k^5 of points that are singular for S_1 . To each of the points of k^5 corresponds a plane pencil of straight lines l . The lines l associated to these singular points, form a congruence $K(5,5)$.

As a straight line of any bilinear congruence of C passes through each point of k^5 , k^5 lies on all surfaces Ω^3 .

A singular line l , i. e. a generatrix of ϱ^5 , cannot intersect a surface Ω^3 in a point that is not singular for S_1 , as the line in S_1 associated to this point, i. e. l , does not cut the line r corresponding to Ω^3 . Consequently each singular straight line has three points in common with k^5 . This ensues also from the fact that according to § 2 the straight lines l associated to points P of a singular straight line, form a cubic scroll ϱ^3 which must consist of three plane pencils, so that each singular line contains three singular points.

Inversely any straight line t cutting k^5 three times, must be a singular line l for S_1 . For the surface ϱ^3 corresponding to this line, is formed by the three plane pencils that correspond to the points of intersection with k^5 , so that to the other points of t a constant ray is associated which must coincide with t .

The scroll ϱ^5 of the singular straight lines consists accordingly of the trisecants of the curve k^5 .

The trisecants of k^5 passing through an arbitrary point A of this curve, lie in the plane pencil (A, α) of the lines l of C through this point. When A is chosen arbitrarily, the generatrices of (A, α) have a conic of points P ; in this case however the point A is associated to any generatrix of (A, α) , so that the generatrices of (A, α) contain two straight lines that are singular for S_1 , and belong to the generatrices of ϱ^5 . Through any point of k^5 there pass therefore always two of its trisecants.

The curve k^5 is a double curve of the surface of its trisecants.

Two trisecants of k^5 cannot intersect each other outside k^5 , as in this case the plane through these two lines would contain six points of k^5 . A plane section of ϱ^5 has consequently five double points.

The surface ϱ^5 is therefore of the genus one.

The straight lines l associated to the points P of a chord k of k^5 , form a plane pencil w_k as the two plane pencils of straight lines l corresponding to the points of intersection of k and k^5 , split off from the surface ϱ^5 corresponding to an arbitrary straight line. As outside this curve k cuts one trisecant of k^5 , w_k contains one trisecant of k^5 .

Inversely to a plane pencil of lines l containing one trisecant of k^5 , there corresponds a straight line of points P cutting k^5 twice. For in this case a straight line which cuts k^5 three times, splits off from the conic associated to an arbitrary plane pencil of C which intersects k^5 five times. Hence the number of bisecants of k^5 through a point P is equal to the number of plane pencils through a line l which contain at the same time a generatrix of ϱ^5 , that is five.

The number of apparent double points of k^5 is five and the genus of this curve is consequently one.

The curve k^5 cuts resp. five and ten generatrices of a plane pencil and of a scroll of lines l . Hence:

The conic k^3 associated to a plane pencil of C , and the curve k^4 corresponding to a scroll of straight lines l , have resp. five and ten points in common with k^5 .

We remark also that the point P associated to a line l , may be determined by constructing in a plane α through l the conic k^3 which cuts k^5 five times. Besides in the vertex A of the plane pencil of C in α , this conic must cut l in the point P corresponding to l . Hence:

The conics k^3 cutting k^5 five times and intersecting a straight line of C twice, all pass through the point P associated to this line.

§ 4. Starting from a twisted curve of the fifth order and the genus one, k^5 , we shall now construct a system S_3 which has the properties of the system that we until now supposed to exist and of which k^5 is the locus of the singular points.

In the same way as every twisted quintic, k^5 lies on a cubic surface Ω_1^3 . We shall make use of the simplest representation of Ω_1^3 on a plane V , which has in V six singular points F_1, \dots, F_6 , to which resp. six crossing straight lines f_1, \dots, f_6 of Ω_1^3 are associated. If e.g. we assume in V a curve k'^5 of the fifth order that has double points in F_1, \dots, F_6 , there corresponds to it on Ω_1^3 a curve of the fifth order and the genus one. For the curve assumed in V has five points that are not singular for the representation, in common with the image of a plane section of Ω_1^3 , i.e. a cubic through F_1, \dots, F_6 .

The image in V of the intersection k^9 of an arbitrary cubic surface Ω_3^3 with Ω_1^3 is a curve k'^9 of the ninth order which has triple points in F_1, \dots, F_6 . The curve k'^9 is therefore completed into a k'^9 by a rational quartic k'^4 that has a triple point in F_6 and single points in F_1, \dots, F_5 . As consequently a given curve k'^5 together with any individual of a linear system of ∞^3 curves k'^4 , is the image of the base curve of a pencil of surfaces Ω^3 all passing through k^5 which contains Ω_1^3 , the surfaces of the third order through k^5 form a linear system Σ_4 of ∞^4 individuals.

A curve k'^4 has in common with k'^5 ten points that are not singular for the representation of Ω_1^3 on V . Two surfaces Ω^3 of Σ_4 have therefore besides k^5 another rational curve of intersection of the fourth order k^4 , resting on k^5 in ten points.

k^5 is a double curve of the surface of its trisecants. For the projection of k^5 out of one of its points on an arbitrary plane, a curve of the order four and the genus one, has two double points and through such a point there pass accordingly two trisecants of k^5 . Further this surface has in common with Ω_1^3 five straight lines that are represented on the five straight lines of V which join F_6 and the other five points F_i ; hence the intersection of the surfaces is of the order fifteen, so that the surface of the trisecants is a surface of the fifth order Q^5 .

Σ_4 contains one surface Ω^3 to which belongs an arbitrary given straight line r . This surface is the locus of the ∞^1 individuals of the ∞^3 conics k^2 intersecting k^5 five times and cutting r twice. For seven points of intersection of such a conic k^2 and Ω^3 may at once be indicated, so that any conic k^2 of which the plane passes through r , lies on the surface Ω^3 which contains r .

The conics k^2 which cut r twice, define therefore on this straight line an involution I , so that there are two conics k^2 touching r (in the double points of I).

Σ_4 further contains one monoid that has its vertex in an arbitrary given point P . This surface Ω^3_P is the locus of the conics k^2 through P . It contains the five bisecants of k^5 through P , as each of these, together with one trisecant of k^5 , forms a conic k^2 through P . Besides these five straight lines there lies on Ω^3_P one more straight line l through P which does not cut k^5 . For the quadratic cone of the tangents of Ω^3_P in P has in common with this surface six straight lines through P and the ten points of intersection of the cone with k^5 lie on the five bisecants.

The planes of the conics k^2 through P have in common with Ω^3_P one more straight line through P which does not intersect k^5 , and pass therefore through l . Inversely each conic k^2 that intersects l twice, must lie on Ω^3_P and passes therefore through P . For a straight line l corresponding to a point P the involution I is accordingly parabolic. The two conics k^2 touching l , coincide in a conic through P .

Besides the complex of the lines l there is also a linecomplex of the fifth order for which the involution I is parabolic. Let us consider a straight line a which cuts k^5 once. A conic k^2 cutting a twice, must pass through the point of intersection of a and k^5 , because else the plane of k^2 would have six points of intersection with k^5 . Through each point P of a there passes one such a conic k^2 , which is the intersection of Ω^3_P and the plane that passes through a and the straight line l corresponding to P . Also for a line a we have, therefore, only one point where it is touched by a conic k^2 .

With a view to determining the order of the complex of the lines l , we take a plane pencil (P, φ) of lines r and investigate the locus of the points where conics k^2 touch these straight lines r . This is a curve which cuts each straight line of (P, φ) twice besides in P and which has a double point in P . The tangents at this double point are at the same time the tangents of Ω^3_P in P which lie in φ . To this curve, which is accordingly of the fourth order, out of its double point P six tangents can be drawn and these are the straight lines for which the involution I is parabolic. As the plane pencil (P, φ) contains five lines a , one line l belongs to (P, φ) , so that the complex C of the lines l is linear.

C contains the surface q^5 of the trisecants t of k^5 . For if we choose P on a straight line t , Ω^3_P becomes the surface of the bisecants of k^5 which cut t and which, together with t , form there-

fore conics k^2 through P . For the surface of the bisecants of k^5 intersecting an arbitrary straight line, is of the fifteenth order, as it has the directrix as a five-fold line, and has ten generatrices in a plane through the directrix. If we take a trisecant t of k^5 as directrix, three cones of the fourth order through t are split off from this surface, so that there remains a cubical surface with t as a double line. The planes of the conics k^2 containing P all pass through the line t , which is therefore associated to P as a line l .

Consequently if k^5 is not degenerate, C is a general linear complex. For if C were special, the axis of C would be a directrix of q^5 and even a multiple directrix, as q^5 is not rational. But outside k^5 two trisecants of this curve cannot cut each other.

We remark also that a trisecant t corresponds to each of its points P as a line l .

To a point P of k^5 an infinite number of straight lines is associated. These form the plane pencil of C that has P for vertex and that is defined by the two trisecants of k^5 through P . For any of the lines of this plane pencil the associated point P must lie in the point of intersection with k^5 . If we choose P outside k^5 and if this point approaches k^5 , $\Omega^3 P$ is transformed into the surface formed by the conics k^2 passing through a given point of k^5 and touching at this point a plane through the tangent to k^5 . Hence there correspond indeed to a point P of k^5 ∞^1 monoids $\Omega^3 P$ that have their vertices in P , and the straight lines l of these monoids form the plane pencil of the straight lines of C through P .

The line elements (P, l) of this \S form indeed a bilinear system of ∞^3 individuals for which k^5 is the locus of the singular points P and q^5 the scroll of the singular lines l .

A bilinear system of ∞^3 line elements (P, l) may always be derived from a twisted curve k^5 of the genus one by associating to each point P the line l through P which does not cut k^5 , of the monoid of the third order that passes through k^5 and has its vertex in P , or, what amounts to the same, by associating the centre of the parabolic involution that is defined on lines l which do not cut k^5 , by the conics intersecting k^5 five times, to these lines l . Inversely in the way indicated a bilinear system of ∞^3 line elements may be derived from any curve k^5 of the genus one.

From the representations of a cubic surface on a plane used in the beginning of this \S , there ensues that ∞^5 twisted quintics of the genus one lie on any given cubic surface. As there lie ∞^{12} cubic surfaces in space, and through any k^5 of the genus one there

pass ∞^4 cubic surfaces, there lie in space ∞^3 curves k^3 of the genus one.

There are, accordingly, ∞^3 bilinear systems of ∞^3 line elements.

§ 5. There are ∞^{15} bilinear systems S_i of ∞^3 line elements for which the complex of the lines l coincides with a given linear complex C . This may be proved by the aid of the representation of NÖTHER¹⁾ of the rays l of C on the points Q of space. For this representation there is one cardinal ray l_1 in C to which all the points Q of a plane V are associated and there is one conic k'^2 of singular points Q in V , to each of which a plane pencil of C containing l_1 corresponds.

To a scroll in C of the order v which has a v -fold line in l_1 , a curve corresponds of the order $v-v$ which cuts k'^2 in $v-2v$ points. Inversely a curve of the n^{th} order of points Q , intersecting k'^2 in s points, is associated to a scroll in C of the order $2n-s$ which has in l_1 an $(n-s)$ -fold line.

A congruence (μ, μ) with a ϱ -fold line in l_1 is represented on a surface of the order $2\mu-\varrho$ of which k'^2 is a $(\mu-\varrho)$ -fold conic, and to a surface of the m^{th} order of points Q containing k'^2 as an m_1 -fold conic, a congruence of rays $(m-m_1, m-m_1)$ is associated that has an $(m-2m_1)$ -fold line in l_1 .

Now let us assume a curve k'^5 of the genus one, formed by points Q , which cuts k'^2 five times. This curve is the image of a scroll φ^5 of the order five and the genus one the generatrices of which belong to C .

Let us now consider the surface formed by the bisecants of k'^5 which intersect k'^2 . This surface has k'^2 as a five-fold and k'^5 as a three-fold curve and is a surface of the tenth order φ^{10} . For k'^2 cuts ten times outside k'^5 the surface of the fifteenth order of the bisecants of k'^5 that cut a given straight line, which surface has k'^5 as a quadruple curve.

To φ^{10} there corresponds a congruence $K(5, 5)$ formed by the plane pencils of C that contain two lines of φ^5 . The vertices of these plane pencils form accordingly the double curve of φ^5 , which is of the fifth order; for in a plane there lie five generatrices of the congruence corresponding to φ^{10} , hence also five vertices of plane pencils of this congruence. As a point of k'^5 carries three generatrices of φ^{10} , the straight lines of φ^5 are trisecants of k'^5 . Inversely each trisecant t of k'^5 lies on φ^5 , because six points of intersection of

¹⁾ "Zur Theorie algebraischer Functionen", Gött. Nachrichten 1869.

t and φ^5 may be indicated, and φ^5 is consequently the surface of the trisecants of k^5 . As a point of k^5 carries two trisecants, this curve is of the genus one. As a rule it is not degenerate. For if k^5 consisted of a biquadratic curve of the first kind and a line of intersection of this curve, C would be a special linear complex, and for any other degeneration of $k^5 \varphi^5$, and accordingly k'^5 , would be degenerate.

Of the bilinear system S_3 of ∞^3 line elements which according to § 5 may be derived from k^5 , C is the complex of the lines l . Else the surface φ^5 would be common to two linear complexes, and as in this case it would belong to a bilinear congruence, it would have two straight directrices, which cannot be the case, even if two straight lines belonged to k^5 . For if e.g. k^5 degenerated into a twisted cubic with an intersecting line and a bisecant, also the bisecants of the cubic which meet the intersecting line, would belong to φ^5 .

§ 6. If we associate to each point P corresponding in S_3 to a line l , the point Q which is conjugated to the same straight line by a representation of NÖTHER, we get ∞^3 pairs of points (P, Q) which define a birational transformation in space. The point P of the line l_1 , which we shall call P_1 , is a cardinal point for this transformation. The corresponding points Q form the plane V . Further k^5 is a curve of singular points P . To each point of k^5 there corresponds a straight line of points Q which cuts k'^3 . The straight lines associated to the points of k^5 , form the surface φ'^{10} .

There are two curves of singular points Q , namely k'^3 and k'^5 . To a point of k'^3 the points P of a plane pencil of C containing l_1 are associated which form a conic k^3 through P_1 . The conics k^3 corresponding to the points Q of k'^3 , form the monoid $\Omega^3 P_1$ that has its vertex in P_1 . To the points Q of k'^5 are associated straight lines of points P that form the surface φ^5 .

If P moves on a straight line, l describes a cubic scroll which contains five generatrices of φ^5 and Q accordingly describes a cubic which cuts k'^3 three times and k'^5 five times. To a plane of points P there corresponds a congruence $(2, 2)$ of lines l containing φ^5 , hence a biquadratic surface of points Q of which k'^3 is a double curve and which contains k'^5 .

If Q moves on a straight line, l describes a scroll containing l_1 and P therefore a rational quartic that passes through P_1 and intersects k^5 in ten points. To a plane of points Q a bilinear congruence of lines l is associated containing l_1 , hence a cubic surface of points P through P_1 containing k^5 .

The pairs of points (P, Q) accordingly define a birational transformation (3, 4)¹⁾.

§ 7. A curve of the n^{th} order which cuts k^5 m times, intersects a surface Ω^3 in $3n-m$ points that are not singular for S_1 and meets $5n-2m$ generatrices of φ^5 outside k^5 . Hence:

The lines l associated in S_1 to the points P of a curve of the n^{th} order that cuts k^5 m times, form a scroll of the order $3n-m$ which has $5n-2m$ generatrices in common with φ^5 .

If inversely we consider a scroll of the order v that has μ generatrices in common with φ^5 , we get by making v and μ resp. equal to $3n-m$ and $5n-2m$ and by solving n and m out of these equations:

The points P corresponding in S_1 to the lines l forming a surface of the order v which has μ generatrices in common with φ^5 , form a curve of the order $2v-\mu$ which cuts k^5 in $5v-3\mu$ points.

A surface of the order p containing k^5 as a q -fold curve, is cut by a conic k^2 and a generatrix of φ^5 resp. in $2p-5q$ and $p-3q$ points that are not singular for S_1 .

To the points P of a surface of the order p with k^5 as a q -fold curve, there correspond accordingly in S_1 the lines l of a congruence $(2p-5q, 2p-5q)$, of which the generatrices of φ^5 are $(p-3q)$ -fold lines.

Inversely it is easily seen that

To a congruence (π, π) of lines l containing the generatrices of φ^5 as π -fold lines, a surface of points P is associated which is of the order $3\pi-5\pi$ and has k^5 as a $(\pi-2\pi)$ -fold curve.

Several applications can be made of the representation defined by S_1 of the rays of C on the points of space. Let us for instance try to find the number of the conics which cut k^5 five times and which meet besides three given straight lines r . These conics are the representations of the plane pencils of C which contain one straight line of each of the three surfaces φ^3 corresponding to the lines r and which have accordingly their vertices in the 27 points of intersection of these three surfaces.

There are 27 conics intersecting five times a twisted quintic of the genus one and cutting besides three given straight lines.

§ 8. Finally we determine the scrolls belonging to C that are associated to the straight lines of a cubic surface Ω^3 which is the locus of the points P of the lines l intersecting an arbitrary straight line r , hence also the line r' associated to r relative to C .

¹⁾ STURM: "Geometrische Verwandtschaften", IV p. 371.

The straight lines r and r' , which both lie on Ω^3 , are the images of the surfaces φ^3 and φ'^3 corresponding resp. to these lines.

Further the five lines t of φ^5 that are singular for S_1 which cut r , belong to Ω^3 as to each of these lines all its points are associated as points P . Besides r these lines also cut r' , and they are trisecants of k^5 .

As the line t belonging to the plane pencil of C which has the point of intersection of r with a line t as vertex and of which the plane passes therefore through r' , splits off from the associated conic, this plane pencil contains a straight line of points P cutting k^5 twice and cutting r' . Accordingly five bisecants of k^5 intersecting r' , lie on Ω^3 . In the same way we find on Ω^3 five bisecants of k^5 which cut r and which are associated to the plane pencils of C that have the points of intersection of r' and φ^5 as vertices.

Finally for a scroll with r and r' as directrices containing three generatrices of φ^5 , and belonging therefore to C , three trisecants of k^5 split off from the associated quartic. Such a scroll is represented on a straight line which cuts k^5 once, but has no point in common with r and r' . On Ω^3 there lie ten lines of this kind.

In this way the images of the 27 straight lines of Ω^3 are found.

If the straight line r belongs to C and is accordingly a line l , we have to do with a monoid Ω^3_P that has the point P of l as vertex. In this case r and r' coincide with l . Also the straight lines that were associated to the ten plane pencils of C which had their vertices in the points of intersection of r and r' with φ^5 , coincide in pairs in five lines through P , as all these plane pencils contain l . These five lines are the bisecants of k^5 through P . Further there lie on Ω^3_P the five trisecants of k^5 cutting l , and the ten straight lines belonging to scrolls of C which cut k^5 once and which have no point in common with l .

Zoology. — "*On the Food of Madreporaria.*" By Dr. H. BOSCHMA.
(Communicated by Prof. C. PH. SLUITER.)

(Communicated at the meeting of November 24, 1923).

The data available in the literature regarding the nature of the food of Madreporaria are still very scanty. We are told, indeed, in many publications on the biology of reef-corals, that the food of these animals consists of planctonorganisms. Most often, however, these statements are not based upon researches with the animals themselves on the digestive phenomena or on the nature of the food. This renders the statements entirely valueless.¹⁾

So far as I have been able to ascertain, this dictum is not applicable to five researchers (GARDINER, DUERDEN, CARPENTER, VAUGHAN and WALTHER): their data regarding the nature of the food of Madreporaria, or regarding the mode of ingestion are derived from a previous investigation of these phenomena in the polyps themselves.

A number of GARDINER's publications²⁾ contain data on the nutrition of reef-corals. According to GARDINER the food of these animals consists chiefly of commensal algae (zooxanthellae), which occur in large quantities also in the endoderm. Many species obtain their food only by means of these algae. In about 1 or 2 percent of the preserved polyps of *Pocillopora* and *Astraea* organic remains of foreign origin were found (GARDINER 1903), which proves that these corals sometimes ingest foreign organisms, although in normal circumstances they feed only on zooxanthellae.³⁾

¹⁾ Instances of it may be found in: W. SAVILLE KENT, *The Great Barrier Reef of Australia*, London 1893.

E. WOLF, *Korallenriffe*. Handwörterb. d. Naturw. 1914.

²⁾ J. STANLEY GARDINER, *The Building of Atolls*. Proc. 4. Int. Congr. of Zoology, 1899.

— On the Rate of Growth of some Corals from Fiji. Proc. Cambr. Phil. Soc. Vol. XI, 1902.

— The Maldive and Laccadive Groups, with Notes on other Coral Formations in the Indian Ocean. The Fauna and Geogr. of the Mald. and Lacc. Arch. Vol. I Part. III 1902, p. 320 and Part. IV 1903, p. 421.

— The Formation of Coral Reefs. Nature, Vol. LXIX, 1904.

³⁾ HICKSON's suggestion (Coelenterata & Ctenophora in: *The Cambridge Natural History*, 1906) that reef-corals derive perhaps in some cases a considerable part

DUERDEN¹⁾ found zooxanthellae (yellow cells) in the endoderm-cells of the polyps of all the species of West-Indian Madreporaria examined by him, with the exception of *Phyllangia americana* and *Astrangia solitaria*. These yellow cells also occur in the interior canals of *Madrepora* and *Porites*, but DUERDEN maintains emphatically, that they never occur free in the gastric cavity of the polyps, except in the larval stages (1902, p. 417). According to DUERDEN the food of the reef-corals consists of small planctonorganisms. The occurrence of zooxanthellae in the endoderm of the reef-corals is not a matter of necessity, seeing that colonies of *Oculina*, *Cladocora* and *Agarcia*, living in shady places may lose their zooxanthellae, which generally occur in large masses in colonies of the same species, and yet live a healthy life outwardly.

In a subsequent publication²⁾ DUERDEN demonstrated that the mucus secreted on the surface of coral polyps plays a prominent part in the nutrition of these animals. Small objects falling down upon this layer of mucus, are imbedded in this substance, and later on the mucus is ingested through the mouth, after which the particles of food contained among the objects, are digested. These researches were carried out with species of *Fungia* and *Favia*. Meat of crabs and other animal food, also extracts of animal matter, were ingested by these corals, when brought within reach of the oral surface of the polyps. Data concerning the nature of the food in normal conditions are not found in this publication.

The way, in which *Isophyllia* ingest food, has been studied by CARPENTER³⁾ who fed the polyps with an extract of meat. According to this author the normal food of these corals consists of small planctonorganisms, captured by the tentacles and afterwards digested in the gastric cavity by the mesenterial filaments.

VAUGHAN⁴⁾ has examined in elaborate experiments the mode of ingestion of various reef-corals. On the reefs he observed that specimens of *Dendrogyra cylindrus*, *Maeandra clivosa* and *Siderastrea siderea*

of their food from their symbiotic zooxanthellae, is probably founded upon GARDINER's data. But HICKSON denies the possibility of reef-corals that feed exclusively on zooxanthellae.

¹⁾ J. E. DUERDEN, West Indian Madreporarian Polyps. Mem. Nat. Ac. Sci. Vol. VIII, Washington 1902.

²⁾ J. E. DUERDEN, The Rôle of Mucus in Corals. Quart. Jour. Micr. Sci. Vol. XLIX, 1906.

³⁾ F. W. CARPENTER, Feeding Reactions of the Rose Coral (*Isophyllia*) Proc. Amer. Ac. Arts Sci. Vol. XLVI, 1910.

⁴⁾ T. WAYLAND VAUGHAN, Studies of the Geology and of the Madreporaria of the Bahamas and Southern Florida. Carnegie Inst. Washington. Yearbook no. 11, 1912.

had caught small medusae, belonging to the genus *Limuche* and that a specimen of *Maeandra areolata* had consumed all the soft parts of a small crab. In his extensive experiments VAUGHAN used meat of crabs and other animals and also extracts to stimulate the polyps. Animal substances, solid as well as liquid, were relished, diatoms were not. Diatoms soaked in an extract of meat were taken up by the polyps, but afterwards the diatoms were discharged undigested. VAUGHAN concluded from this that the food of corals consists solely of animal matter (p. 161). Excepting the cases above-quoted, in which medusae and crabs are named as the food of corals, no mention is made in this publication of the food that occurs in normal cases in the gastric cavities of the polyps.

In a later publication VAUGHAN¹⁾ again maintains that the food of corals consists of animal organisms, notably of small swimming and floating plancton animals. In this connection he raises the supposition that the limit of the vertical distribution of the coral-fauna of the shallow water (46 m.) is determined by the quantitative decrease of these planctonorganisms at that depth.

Concerning zooxanthellae MAYER²⁾ observes: "Certainly they do not directly supply nourishment, for corals refuse all plants as food" (p. 28). MAYER maintains that the food of corals is exclusively animal food and bases his pronouncement on the above researches by VAUGHAN and on DUERDEN's³⁾ data who kept his colonies of *Siderastrea radians* during a long space of time in perfect health in an aquarium, by feeding them with the meat of crabs and other animals.

WALTHER⁴⁾ reports that in fresh-conserved corals chlorophyll can be established spectroscopically. In addition he points out that he could not find any tentacles in many forms of corals from the islands in the Bay of Batavia and that no planctonic food occurs inside the polyps of these corals. WALTHER concludes from this that the nutrition of many reef-corals occurs through chlorophyll-assimilation. These statements have, however, not been worked out, neither did the author name the reef-corals upon which he had worked.

¹⁾ T. WAYLAND VAUGHAN, Corals and the Formation of Coral Reefs. Smithsonian Institution. Annual Report for 1917. Washington 1919.

²⁾ A. G. MAYER, Ecology of the Murray Island Coral Reef. Carnegie Inst. Washington. Dep. of Marine Biology, Vol. IX, 1918.

³⁾ J. E. DUERDEN, The Coral *Siderastrea radians* and its Postlarval Development. Carnegie Inst. Washington. Pub. no. 20, 1904.

⁴⁾ J. WALTHER, Allgemeine Palaeontologie. Geologische Fragen in biologischer Betrachtung. I. Teil, Berlin 1919.

From November 1920 to September 1922 I have been examining a large number of living coral-polyps in order to establish the nature of the food of these animals in normal circumstances. I made my researches especially in the island of Edam, but I have studied corals also in other islands in the Java Sea and Sunda Strait (Pulu Kelapa and the surrounding islands, Noordwächter, Huisman's Eil. near Sebesi). During the Danish Expedition to the Kei Islands, I have been able to gather further data concerning the nutrition of corals, in shallow water as well as in deeper water (± 250 m.).

Now as far as the reef-corals are concerned my results square fairly well with GARDINER's: the food of these animals consists mainly of zooxanthellae. GARDINER's observations on the nutrition of reef-corals have been published as brief notices in memoirs chiefly devoted to other subjects; this is perhaps why they are little known. Moreover in a later publication¹⁾ he is less decided in his opinion that zooxanthellae generally constitute the most important part of the food of reef-corals. Although he states that most probably a large number of zooxanthellae are ingested by coral-polyps when they require food, he also mentions that it is supposed that coral-polyps catch and digest the small organisms occurring in superficial water of the sea. It may be of interest, therefore, to communicate my results, also because they are different from the results of most of the researchers quoted above.

The endoderm of nearly all Madreporaria from shallow water contains large quantities of zooxanthellae. I found these algae in all species of the following genera: *Madracis*, *Seriatopora*, *Pocillopora*, *Stylophora*, *Euphyllia*, *Cyphastrea*, *Echinopora*, *Galaxea*, *Favia*, *Favites*, *Goniastrea*, *Leptoria*, *Maeandra*, *Hydnophora*, *Mussa*, *Symphyllia*, *Merulina*, *Fungia*, *Herpolitha*, *Polyphyllia*, *Halomitra*, *Pavona*, *Psammocora*, *Turbinaria*, *Montipora*, *Acropora* (= *Madrepore*), *Goniopora*, and *Porites*. In Madreporaria the zooxanthellae seem to be restricted to certain genera: when they occur with one species they are also found in other species of the same genus and conversely there are other genera of which none of the species possesses zooxanthellae. Zooxanthellae also occur in Madreporaria from somewhat deeper water (± 50 m.), but these species always belong to a genus that is also represented by species on the reefs in shallow water. Contrary to HICKSON's²⁾ statement that these algae do not

¹⁾ J. STANLEY GARDINER, The Shore, in: Science of the Sea, edited by G. HERBERT FOWLER, London 1912.

²⁾ loc. cit. p. 874.

or hardly ever occur in *Pocilloporidae*, I found zooxanthellae in large quantities in all the species of the genera *Pocillopora* and *Seriatopora* that I examined.

The zooxanthellae (yellow cells) of the reef-corals are spherical, dark-yellow, unicellular algae from 7—10 μ in diameter. It is difficult to decide whether the colour is confined to definite chromatophores. In the living zooxanthellae the whole cell is of an evenly yellow colour and in fixed material I have not observed any single chromatophores. The living yellow cells contain a highly refractive granule (sometimes two), apart from that they present nothing particular. This granule stains a brownish-violet with iodine, which reaction will take place more readily when the cells have first been treated with an acid. This staining method implies that the refracting granule contains an amyloid assimilation-product. The reaction proves that this substance is different from the starch of higher plants, which is of a much darker blue after treatment with iodine. The nucleus of the zooxanthellae, which is not recognizable in the living cells, becomes distinctly visible, after the addition of acetic acid, as a granular body usually of slightly smaller dimensions than the assimilation-product. Addition of fuchsin also reveals the nucleus of zooxanthellae as a corpuscle of light red coloration.

In fixed material some further particulars are to be noted after treatment of the yellow cells with nuclear stains. Among the various staining methods I got the best results with HEIDENHAIN'S iron-haematoxylin method; safranin and light-green also yielded good results.

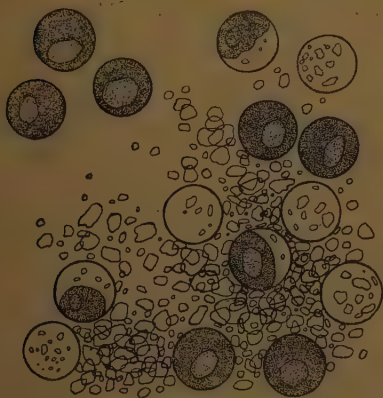


Fig. 1.

The nucleus contains a number of highly stainable granules (Fig. 2). Of the intensely refractive corpuscle in the living yellow cells only the central portion is stained. The outer layers of this corpuscle, the assimilation-product proper, now remain unstained, so that the central portion, the pyrenoid, becomes distinctly visible. Furthermore the protoplasm reveals a considerable number of vacuoles in many preparations ¹⁾.

¹⁾ A short description of the zooxanthellae is also given by DUERDEN (1902) and MATTHAI (A Revision of the Recent Colonial *Astraeidae* possessing distinct Corallites. Trans. Linn. Soc. London (2) Zool. Vol. XVII, 1914). In the figures of these publications the nucleus and the pyrenoid with the assimilation-product are distinctly visible. In DUERDEN'S figures a few smaller granules have moreover

When investigating the nutrition of coral-polyps in normal conditions, I have closely examined the contents of the gastric cavity in a great number of polyps of all the species of *Madreporaria* that I found on the reefs. In the cavity there are generally partially digested food-rests consisting of a mucous mass, that can easily be removed with a fine pipette. When reef-corals are being fixed they often discharge the food-rests through the mouth which accounts for the fact that, as a rule, little information can be got on the nutrition of corals from preserved material. In all the true reef-corals examined (i.e. the species containing zooxanthellae in their endoderm) the mucous substance from the gastric cavity contained a large number of undigested yellow cells, quite similar to those in the endoderm-cells. Besides those there were generally a few cells which were partially decoloured (partially digested zooxanthellae) and always a large number of colourless spherules of the size of zooxanthellae, but all varying as to their contents. (Fig. 1). I could observe all stages intermediate between intact yellow cells and these colourless spherules, so that the latter are undoubtedly zooxanthellae in an advanced stage of digestion. That they retain their spherical shape so long points to the fact that the wall of the zooxanthellae is highly resistant. Besides the above-named corpuscles distinctly recognizable as yellow cells and their products of decomposition, the contents of the gastric cavity of reef-corals contains always a good many smaller colourless granules of irregular shape, probably composed for the greater part of further products of decomposition of the zooxanthellae. Furthermore the mucus of the coelenteron contains almost always nematocysts and portions of them.

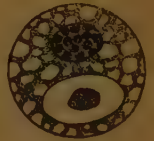


Fig. 2.

In most reef-corals the food remnants contain only exceptionally other organisms or fragments of them besides zooxanthellae and nematocysts. Sometimes a few diatoms are found in the coelenteron of the forms with small polyps such as species of *Porites*, *Acropora*, *Pocillopora* and *Cyphastrea*, but generally no other organisms than zooxanthellae. The rule is that the quantity of foreign organisms of which there is a certain percentage in the content of the gastric cavity, increases with the size of the polyps. Only in the species of some genera with large polyps (*Fungia*, *Favia*, *Favites*, *Symphyllia*, *Mussa*) do we nearly always find other organisms in the mucus of the gastric cavity, namely Copepods, nauplius larvae, remains of An-

been marked in the protoplasm, which, however do not occur in the zooxanthellae of my material.

nelids, foraminifera, diatoms, *Lingbya* and other algae. Together with these organisms the polyps have generally taken in also detritus such as sponge-spicules and skeletal corpuscles of Holothurians. But still zooxanthellae remain the chief constituent of the food in normal conditions, also in those species in which usually foreign organisms are found in the coelenteron.¹⁾

I examined two species of the genus *Fungia* (*F. fungites* (L) and *F. actiniiformis* Q. & G.) for their capacity to ingest plancton. When placed in a glass and allowed to stand for some time, corals of this species will secrete a layer of mucus at their oral surface. Now plancton-organisms (especially Copepods) were added to the water and presently a large number of them stuck to the layer of mucus. Ultimately the polyp took in the mucus with the organisms piecemeal by the mouth, in the way described by DUERDEN (1906) for another species of *Fungia*.

In living coral polyps it is generally not easy to ascertain where the food is digested. Only with *Favites abdita* (Ell. & Sol.) could I observe that the contents of the coelenteron (an accumulation of mucus with many half-digested zooxanthellae and plancton-organisms a.o. a number of Copepods) could be observed only on the mesenterial filaments. These plugs of mucus, which had no connection with each other, were clearly visible, especially in colonies of this species, which had been standing longer than a day, and of which the mouths of the polyps had opened during the night. Most likely it is, therefore, that the mesenterial filaments in *Favites* play a prominent part in the digestion of food, just as CARPENTER (1910) has demonstrated for *Isophyllia*...

The zooxanthellae in the coelenteron of the reef-corals have as a rule probably been ingested by the mouth of the polyp. This opinion is supported by the following observations: 1. In the mucous layer secreted in *Fungia* on the oral surface many zooxanthellae are always to be found, that afterwards are taken in by the mouth together with the mucous layer and the organisms of foreign origin. Even when this layer has just originated, zooxanthellae are already present; 2. In *Seriatopora* it can always be observed microscopically that some free zooxanthellae move along the branches of the colony across the ectoderm and that finally they are taken in by the polyp's mouth. In the gastric cavity there is a small plug of

¹⁾ It is striking that most often I found in the living coral polyps remnants of food in the gastric cavity and in those remnants zooxanthellae, whereas DUERDEN reports that he never observed zooxanthellae in the coelenteron of the West-Indian *Madreporaria*.

mucus often in circular motion, in which zooxanthellae are clearly distinguishable.

Theoretically two more possibilities must of course be considered: either the zooxanthellae in the coelenteron are derived from the endoderm-cells of the polyp itself, or they have been introduced from the seawater. Now it is a fact, that in the coelenteron of *Dendrophyllia coccinea*, a species that lodges no zooxanthellae in the endoderm, only very rarely a single zooxanthella can be found, also in those polyps living in the proximity of a number of colonies of reef-corals. Now if the latter had taken up the zooxanthellae, which constitute a prominent part of their food, from the seawater, these organisms should necessarily also always be found in the food-rests of *Dendrophyllia*. Seeing that this is not the case, it is probable that the zooxanthellae present in the gastric cavity of the reef-corals were living previously in tissues of the corals themselves.

The infection of the young larvae with zooxanthellae takes place in the mother-animal. DUERDEN (1902) showed already that the young planulae lodge many yellow cells. I found the same in the newly hatched planulae of *Fungia actiniformis*, which will sometimes contain as many as 180 zooxanthellae. So long as the eggs are still attached to the mesenteries, zooxanthellae are found, indeed, in their proximity, but they themselves have not yet been infected. Developmental stages previous to the planulae I have not been able to find. Therefore I cannot say in which stage infection takes place. This infection of the young stages implies that the association with the yellow cells is greatly to the benefit of the coral-polyps. The phenomenon is an instance of symbiosis¹⁾. It is difficult to decide whether this is of a mutualistic nature, or whether the association of the two organisms is to be considered as a case of parasitism, as PRATT²⁾ thinks, in which the coral-polyps live upon the zooxanthellae. The large quantities of symbionts, present in a living state in the endoderm are rather indicative of a mutualistic association.

Because they require light for their photosynthesis of carbohydrates, zooxanthellae cannot live at a lower depth than 50 to 70 m. This factor chiefly determines the vertical distribution of reef-corals, as GARDINER also supposed (1899).

¹⁾ P. BUCHNER, Tier und Pflanze in intrazellulärer Symbiose. Berlin 1921.

²⁾ E. M. PRATT, The Digestive Organs of the Alcyonaria and their Relation to the Mesogloea Cell Plexus. Quart. Jour. Micr. Sci. Vol. XLIX 1906. In this publication and in others by the same writer the yellow cells are invariably termed „zoochlorellae“. However, judging from their description and from the figures they are zooxanthellae.

Zooxanthellae of the same shape, structure and colour as in reef-corals also occur in the Hydrocorallid *Millepora* and in the Alcyonarian corals *Tubipora* and *Heliopora*. The polyps of the species of these genera also feed chiefly on their zooxanthellae. For other genera of Alcyonaria PRATT¹⁾ has described zooxanthellae not differing in any way from those of the Madreporarian corals. They are also found in the tissues of many Actiniae and Scyphomedusae.

The zooxanthellae occurring in large numbers in *Tridacna* in the light coloured parts of the mantle²⁾, also closely resemble those of the corals. Here also a considerable portion of the food is furnished by the zooxanthellae: in the stomach and the adjoining part of the intestine of *Tridacna* I detected large quantities of zooxanthellae in all stages of digestion.

The zooxanthellae of a species of *Collozoum* in the island of Amboina I compared with those of corals. They are larger than the latter (12—15 μ), of a lighter yellow, and are chiefly distinguished by more than one product of assimilation in each cell. They are completely like the yellow cells of various Radiolaria examined minutely by BRANDT³⁾. According to BRANDT the amyloid substance appears as bodies with a large vacuole; these bodies, however, are massive and possess a central highly stainable grain, a fact, afterwards pointed out by STIASNY⁴⁾. So in this respect the product of assimilation corresponds with that of the zooxanthellae of the corals, in which there is also a central body (pyrenoid) that may be coloured with nuclear stains.

No zooxanthellae are to be found in some species of Madreporaria living in shallow water, sometimes close to the surface, such as *Dendrophyllia micranthus* (Ehrb.) (= *nigrescens* Dana) and *Dendrophyllia coccinea* (Ehrb.)⁵⁾, two species of general occurrence in Amboina and the Kei Islands. Now it is striking that in *D. coccinea* large quantities of yellowish-green corpuscles of irregular shape occur in the endoderm, not to be found in the tissues of reef-corals. In teased preparations of the tissues of the living animal, these

¹⁾ E. M. PRATT, The Alcyonaria of the Maldives. Pt. II. Fauna Geogr. Mald. and Lacc. Arch. Vol. II Pt. I 1903. Compare also the above cited publication.

²⁾ cf. NUSSBAUM-KARSTEN-WEBER, Lehrbuch der Biologie, 2 Aufl. 1914, p. 550.

³⁾ K. BRANDT, Die Koloniebildenden Radiolarien (Sphaerozoöen) des Golfes von Neapel. Fauna und Flora des Golfes von Neapel. 1885.

⁴⁾ G. STIASNY, Zur Kenntnis der gelben Zellen der Sphaerozoen. Biol. Centralblatt. Bd. XXX, 1910.

⁵⁾ The new nomenclature of these species is adopted from C. J. VAN DER HORST, Eupsammidae. Siboga Expedition Monogr. XVIc, 1922.

corpuscles are isolated and assume a globular shape. They are of a granular structure, in some of them one portion stains more deeply, but a nucleus cannot be made out with certainty. Besides these greenish yellow corpuscles the above-named species still contains a finely distributed red pigment in the outer layers. *Dendrophyllia micranthus* has the same greenish yellow corpuscles in the endoderm and, besides, a black pigment instead of the red one of *D. coccinea*. In the gastric cavity of these animals rests are found of small Crustacea, diatoms, foraminifera, Oscillatoria and detritus, such as sponge spicules, but besides these also a number of the greenish yellow corpuscles like those of the endoderm of a fairly rounded shape. Sometimes also a few zooxanthellae can be made out, but only with animals living near other corals that contain zooxanthellae in their tissues.

Now this invites us to conclude that the greenish yellow corpuscles in *Dendrophyllia* play the same rôle as the zooxanthellae in reef-corals. MAC MUNN's¹⁾ researches lend support to this hypothesis. This author demonstrated spectroscopically that in two species of *Dendrophyllia* (*D. nigrescens* and *D. Willeyi*) a chlorophylloid pigment occurs. The greenish yellow colour of the said corpuscles renders it probable that the chlorophylloid pigment is localised here. The fact also that these greenish yellow corpuscles are regularly present in the food, suggests an analogy to the zooxanthellae of reef-corals.

Regarding the nature of the greenish yellow corpuscles there are two possibilities: they are either elements of the tissues of the polyps themselves, or they are symbiotic individual organisms. In the latter case, however, the organisms (algae) are supposed to be highly reduced²⁾. That the yellowish green corpuscles should be formed by the coral-polyps themselves seems to be an untenable hypothesis, if we consider that in all the cases, where formerly animal chlorophyll was recorded, it has been demonstrated afterwards that this chlorophyll was derived from a foreign source. For the present the available data do not enable me to solve this question.

In the tissues of a small *Balanophyllia*, generally met with at the lower surface of large colonies of reef-corals in the Java Sea,

¹⁾ C. A. MAC MUNN, On the Pigments of Certain Corals. Fauna and Geogr. of the Mald. and Lacc. Arch. Vol. I, Part. II, 1902.

²⁾ Cases are known in which symbiotic algae lose entirely their individual character and cannot any longer live without the animal (cf. F. KEEBLE and F. W. GAMBLE, The Origin and Nature of the Green Cells of *Convoluta roscoffensis*. Quart. Journ. Micr. Sci. Vol. LI, 1907).

the same greenish yellow corpuscles occur in large numbers. I have not been able to find any remnants of food in these corals.

In the genera of the Madrepোরaria, of which the species are found only in deeper water, the tissues contain no zooxanthellae¹⁾ Little is known as yet concerning the food of these corals. GRAVIER²⁾ found in the gastric cavity of *Stephanotrochus diadema* rests of a crustacean, fragments of arms of Ophiurids and sand with many foraminifera. Now conclusions on the nature of the food of deep-sea-corals should not be drawn without due consideration. If one finds in the coral-polyps from deeper water only sand with foraminifera, this does not prove that they have ingested this as food, since in the majority of cases the sand has entered into the gastric cavity while the polyps were being dredged up. In some of them I found, besides sand, remains of animals or plants in a mucous substance. These are presumably remnants of the food of the polyps. In the gastric cavity of a *Dendrophyllia* dredged up in the Bay of Amboina between 45 and 90 m. I found the remains of small Crustacea and many diatoms. The food-rests of *Cyathohelia axillaris* (Ell. & Sol.) of Amboina (about 130 m.) contained Copepods, diatoms, and sponge spicules. In *Odontocyathus* sp. from Station 2 of the Danish Expedition to the Kei Islands (± 200 m.) I found in the coelenteron remains of extremities of Crustacea, foraminifera and sponge spicules. Also *Stephanophyllia formosissima* Mos. (same Exp., Stat. 41, 245 m.) contained remains of small Crustacea in the gastric cavity of some specimens. In the gastric cavity of many other specimens of various species many foraminifera occurred, but these had probably entered there during the dredging.

Leiden, November 1923.

From the Zoology Laboratory of the University.

EXPLANATION OF THE FIGURES.

Fig. 1. *Acropora variabilis* (Klunz.). Remnants of food from the gastric cavity of a polyp, with normal and partially digested zooxanthellae. The dotted parts were coloured yellow. $\times 825$.

Fig. 2. Zooxanthella from the endoderm of *Goniopora stokesi* M.—E. & H. Preserved material (alcohol) stained with safranin and light-green. $\times 1950$.

¹⁾ The "zooxanthellae", occurring according to BOURNE (Report on the Solitary Corals collected by Prof. HERDMAN in Ceylon. Rep. Pearl Oyster Fisheries, 1905) in *Heterocyathus* and *Heteropsammia* are cells of a quite different nature belonging to the tissues of the polyps themselves.

²⁾ CH. GRAVIER, Madréporaires provenant des Campagnes des Yachts Princesse-Alice et Hirondelle II. Résult. Camp. Scient. Fasc. LV, Monaco 1920.

Histology. — "*The nervous elements in their relation to connection-tissue cells, in the cornea of the frog's eye*". By Prof. J. BOEKE and G. C. HERINGA.

(Communicated at the meeting of October 27, 1923).

In recent years animal histologists have become more and more convinced, that the old conception of the cells as elementary organisms, indivisible, self-propagating and independent, originating in a direct line from the dividing egg-cell and, even there where they build up the living body, remaining independent units until their death or the death of the organism which they helped to build up, must be revised. As it stands, this conception is insufficient to explain the structure of the living tissues. Both in regeneration experiments as in the phenomena of histogenesis the cells seem to lose a part of its independence as an elementary organism.

Many of them we see in the course of development losing their boundaries and fusing together to form a syncytium. And even when, as seems to be the case in the myocardium of mammals, this syncytium in a later period of development is again differentiated into cells, even here the lines of junction of the cells are bridged across by the muscle-fibrils, and we are by no means sure, that the so-called cellular elements, which we are able with tolerable accuracy to make out in the fullgrown myocardium, are the self-same elements which were seen to constitute the heart-muscle tissue before the coalescing period.

So we see that the cross-striated voluntary muscle-fibres with their immense number of nuclei, formerly supposed generally to be formed by the elongation of a single enlarged cell, are the product of more than one cellular element. Not only they are built up by the joining together, end to end, of a number of cells of the muscle-plate, so as to form a syncytium, within which the striated fibrils make their appearance, but secondly, even more than one segmental muscle-plate may contribute to the formation of a single muscle-fibre, as GODLEWSKI (1) and SUNIER (2) have shown and AGDUHR (3, 4) was able to prove by their plurisegmental innervation, and thirdly, as SUNIER has shown, even mesenchymatous elements may take a part in the formation of the muscle-fibres.

As to the smooth muscle-cells, what we know about their development tends in the same direction. According to the observations of miss Mc GILL (5) the smooth muscle-cells of the elementary canal of the pig, seemingly so distinctly separate as true cellular organisms in the adult animals, are developed from a syncytium of mesenchymatous cells surrounding the entoderm tube. Their myofibrils extend over two or even a number of cells. According to the observations of HERINGA and TEN BERGE (6) the endothelial cells of the blood-capillaries are in protoplasmatic connection with, and form a part of the syncytium of the mesenchymatous elements around them.

The same holds true for the follicle-cells of the ovary, for the Sertoli-cells and the interstitial cells of the testis, for the different forms of connective tissue, as HERINGA has shown by his "Dunkelfeld"-method (7, 8) and last not least, for the elements of the nervous system. For, according to the observations of HELD, during their development they seem to pass through a syncytial period that leaves them by no means the selfsame elements that went into it. As to their later development, it was shown by HELD (9) that the fibres of the neuroblasts do not run free in the interstices between the cells, but that they everywhere follow distinct protoplasmatic paths either of migrant medullary elements or of mesenchymatous cells, until they reach their destination, and both of us (BOEKE 10, 11, 12, HERINGA 13, 14) were able to confirm his statements. In the adult animal too we never find free "naked" nerve-fibres running in the interstices between the cells of the tissues, not even inside the epithelium (BOEKE, 12, 15), and in the process of nerve-regeneration after the cutting of the nerve (BOEKE 10, 11) the same fact stands out clearly. During the process of nerve regeneration after the nerve has been cut, we see a perfect harmony between the elements of the different tissues which build up the path that has to be followed by the regenerating nerve-fibres, in which all the surrounding elements, the sheath-cells, the connective-tissue cells, the elements of the original endorgans are seen taking a part in perfectly harmonious co-operation.

So we see in the adult animal a close connection between the outgrowing axons of the nerve cells, and the surrounding cells of the nerve-sheaths. But if this assumption be true, we may ask, whether the elements, by which during ontogenesis the outgrowing axons of the neuroblasts are surrounded, enclosed, and with which they form a new compound element, the peripheral nerve-fibre, are all of an ectodermal nature (NEAL) or of both an ectodermal and an

mesodermal nature (HELD)? The latter seems to us to be more probable. As was mentioned above, both in the ontogenetic development of the sensory nerve-endings (HERINGA) and in the course of the regeneration process of the motor nerve-endings after cutting of the nerve (BOEKE) there was found a close connection between the outgrowing nerve-fibres and typical connective-tissue cells (mesodermal elements). The same intimate protoplasmatic connection between nerve-fibres and surrounding connective-tissue cells in the adult animal could be demonstrated for the sensory nerve-fibres, which normally innervate the neuro-muscular spindles (BOEKE, 10, 12) and for those sensory nerve-fibres, that are found in the subcutaneous connective tissue (HERINGA 16).

In looking for a tissue, where those statements could be verified in the adult, we came upon the cornea as a structure, in which we were convinced, that, if such a connection really exists, it must be possible to study it very closely and exhaustively, eventually to prove its existence definitely.

For, as is well known, coated with the stratified epithelium and the homogeneous membrane of BOWMAN, upon which the deepest cells of the epithelium rest, the substantia propria of the cornea is composed of bundles of white collagenous fibres arranged in regular laminae, very distinct in the frog's cornea, the direction of the fibres crossing one another at right angles in the alternate laminae. Between the laminae lie the only cellular elements of the substantia propria, the flattened connective-tissue corpuscles. These are branched and united by their processes into a continuous network, lying in the spaces between the laminae. In each layer these cells, called "orthoklone" cells because of the rectangular mode of branching of their processes, form a continuous network, with very regular rectangular meshes (especially in the frog's eye), in connection with the direction of the fibres in the laminae, between which they are extended. According to most authors these flattened cells fill up entirely the spaces between the fibrillar laminae, in which they are lying. But about this question of the spaces ("Saftlücken") in the substantia propria, even in its most modern form (E. MAGNUS, A. STUBEL) we will not enter into discussion here.

The nerves of the cornea pass in from the periphery, losing their myelin sheath as they enter the corneal substance. In the deeper layers of the substantia propria they form a coarse plexus, the primary plexus, with typical lemnoblastic nuclei, lying mostly in the knot-points of the plexus. In nearing the surface of the cornea, the plexus gets finer, in the superficial part of the cornea it forms

a very fine and delicate plexus, the subbasal plexus, without a trace of lemnoblast nuclei.

From out this plexus, well known since the researches of COHNHEIM, KÖLLIKER, ENGELMANN and KUEHNE, and which displays a very characteristic appearance especially in the cornea of the frog's eye with its so very regular arrangement of the connective-tissue fibres, so-called rami perforantes, which also may run separately through the substantia propria, pass through the membrane of BOWMAN, underlying the epithelium, into the epithelial layer. Here a secondary plexus, the subepithelial plexus is formed ¹⁾, immediately under the epithelium which covers the anterior surface, and a terminal plexus of fine fibrils which pass from the subepithelial plexus and become lost between the epithelium-cells. They may be followed into the superficial layer of cells. Of lemnoblastic cells or nuclei no traces are to be found.

The same holds true for the finer part of the nerve-plexus in the superficial layers of the substantia propria; no trace of lemnoblastic nuclei, only a network of very delicate nerve-fibres, running between the connective-tissue layers, the different parts being connected by very delicate threads, passing from one layer of connective-tissue cells to the other.

Long years ago KUEHNE described a close connection, throughout the entire substantia propria, between the nerve-fibres and the adjoining corneal cells („fixe Hornhautkörperchen"), in which he was followed by COHNHEIM, who said in his first communication, „die Angaben KUEHNES in jeder Hinsicht bestätigen zu müssen" but with some exceptions (KÖNIGSTEIN, WALDEYER, CIACCIO), all later authors agree, that such a connection does not exist. Even DOGIEL, who studied the distribution of nerve-fibres in the human cornea by means of methylene blue, found nowhere a nerve-ending in connection with a corneal corpuscle, and COHNHEIM in a later communication took back his first acknowledgment of the observations of KUEHNE. „Da Nervenfäden" says VON EBNER, „und Zellenansläufer an hundert und hundert Stellen sich kreuzen, so hat es zwar oft den Anschein, als ob beide da und dort zusammenhängen, bei möglichst genauer Untersuchung findet man jedoch immer und immer wieder, dass die beiderlei Elemente nur an einander vorbeigehen, und es kommen nur selten Fälle vor, in denen eine bestimmte Entscheidung nicht zu geben ist." (Lehrbuch Kölliker II, p. 792).

¹⁾ This plexus, and the relation of its nerve-fibres to the epithelium cells we intend to discuss in a following communication.

And so, when SCHAEFFER in his textbook of histology gives a picture of the distribution of the nerve-fibres in the substantia propria of

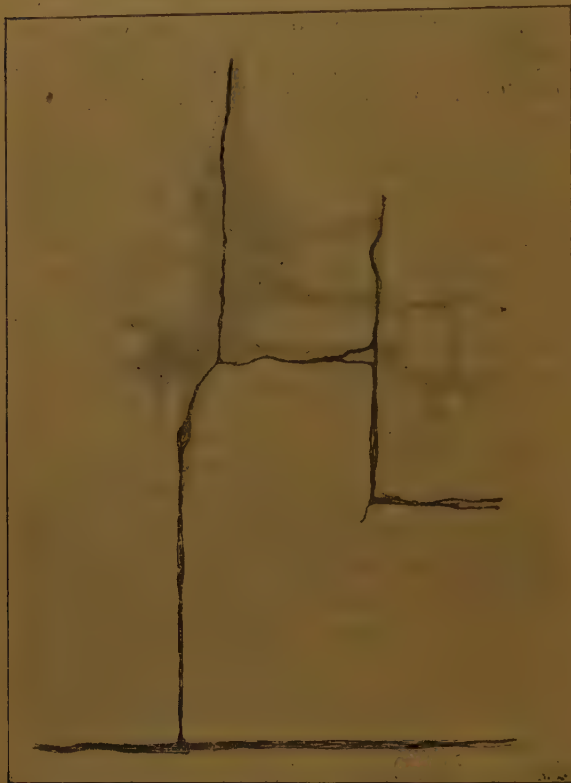


Fig. 1.

the cornea (a picture, which by the way, does not represent the subepithelial plexus, as is stated in the text, but the *subbasal* plexus), he draws the nerve-fibres everywhere as a system of very fine, more or less varicose, threads, ramifying and here and there anastomosing with each other, but entirely independent of the regular system of the processes of the orthoclone corneal corpuscles that are united into a continuous network.

And yet it seems to us, that this conception must be revised

Surely, when we treat the cornea of a frog's eye with chloride of gold after the method of COHNHEIM or LÖWITT, and examine it under a low power, we get a picture of the subbasal plexus corresponding exactly with the one drawn by SCHAEFFER, viz. a system of very fine lines, ramifying at right angles apparently in correspondence with the direction of the white fibres in the adjoining connective-tissue laminae, intermingled with other fibres running in all directions, seemingly entirely independent of the system of the connective-tissue elements. But when we take a preparation of the cornea, treated with chloride of gold after the method of LÖWITT in the best way possible, in which the nerve-fibres are seen as delicate black lines and the connective-tissue cells have taken a dark purple stain, so that we can distinguish even the finest processes and expansions of their protoplasm by their granular appearance and purple colour, and when we examine such a preparation under the highest power (Apochrom. oil-immersion. 2 m.m. comp. oc.) and with the strongest

light, we come to the conclusion, that there exists a very distinct and intimate connection between the nerve-threads and the connect-

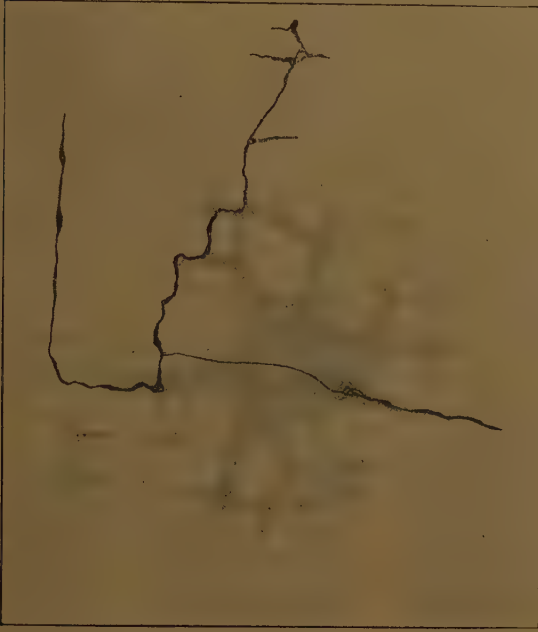


Fig. 2.

ive-tissue cells of the substantia propria. Both there, where the nerve-threads present themselves as straight lines with ramifications running at right angles from the headlines (Fig. 1) and there, where the course of the threads and their ramifications is irregular and curved (Fig. 2, 3), we see everywhere the delicate black lines surrounded by the protoplasmic granules of the connective-tissue cells, so that they are running intraprotoplasmically.

In most cases they are connected only with the cellprocesses, but often they are seen transversing the thickened part of the protoplasm forming the cellbody, and it is here, that the intimate connection with the protoplasm of the cells, their intraprotoplasmatic position, could be made out most accurately.

Thanks to the regular course of the cellprocesses and the position of the orthoklone cells spread out in one plane between the laminae of the connective-tissue fibrillae, it is possible to follow in a chloride of gold preparation under a high power every ramification of the cellprocesses and every expansion of the protoplasm of the cellbody with the utmost accuracy, and so for example it was clearly visible, that the protoplasm of the corneal cell, in which was imbedded the thin nervous fibre of the figs. 2 and 1, surrounded the thread on all sides, and that the granular protoplasm could be traced uninterruptedly surrounding the delicate nerve-threads there, where they left the cell-body and followed the cell-processes. The nerve fibrillae run inside the protoplasm of the corneal cells, and in this connection we should like to call attention to the analogous case of the muscle-spindles. Here, as it was described so well by SHERRINGTON, we find the axial muscle-fibres completely

surrounded by a large lymph space, bridged across and partially subdivided in many points by extremely tenuous membranes, filaments and strands of syncytial connective-tissue elements. And here it



Fig. 3.

could be stated (BOKKE, 1916), not only that the end-ramifications of the normal nerve-fibres are everywhere enclosed within the protoplasm of these mesenchymatous cells, but even that after the cutting of the nerves during the degeneration phase of the regeneration process the syncytial cells, proliferate, branch and form numerous new connections, so that a typical conducting syncytium is formed, which catches up the ingrowing fibres, encloses them and enables them to reach their destination, the axial muscle-fibres. And secondly we could point at the analogous con-

clusions reached by HERINGA for the sensory nerves of the skin (HERINGA, 1920, 1923) in the adult and during development.

The crucial test, that the nerve-fibres are running intraplasmatically, can only be furnished by cross sections through the cornea, cutting the corneal cells at right angles to the plane in which they are extended. If we only take care to prevent the shrinkage of the collagenous fibres and of the cells, which is only possible by using the gelatine-freezing method of HERINGA, enabling us to make serial sections of 5μ through the cornea, without bringing the tissues in contact with alcohol and paraffin, than we see in BIELSCHOWSKY-preparations not only that the cells of the substantia propria fill up entirely the spaces in which they are lying, but that the nerve fibres are everywhere enclosed in the protoplasm of the connective-tissue cells (fig. 4), mostly lying in the processes of the cells, just as we found them in the foregoing chloride of gold preparations, and even there, where a nerve-thread of the subbasal plexus runs obliquely from one lamina to the other, we always found it surrounded by a thin layer of granular protoplasm. (Fig. 4, z. v.). When studying these transverse sections through the cornea, we are everywhere

struck with a phenomenon, described by both of us in former papers (BOEKKE, Studien zur Nervenregeneration, HERINGA, Bau und Entwicklung des peripheren sensibelen Nervensystems), that the neurofibrillae,

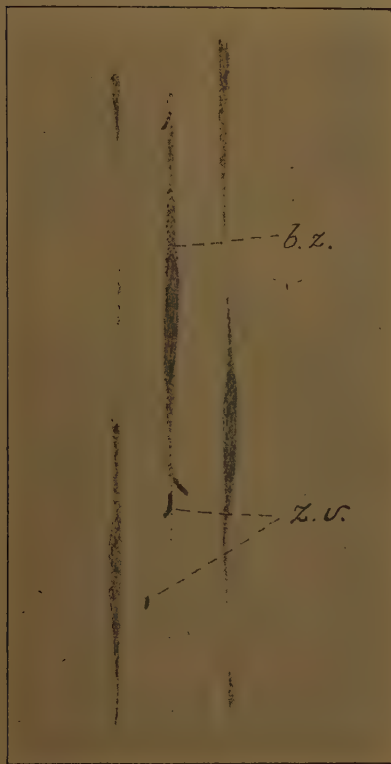


Fig. 4.

Cross section through the substantia propria of the cornea, highly magnified, BIELSCHOWSKY-stain:

b.z. = connective-tissue cells,

z.v. = nerve-fibres, magnified 2100 diameters.

not the case and that they are in reality imbedded in and surrounded by the protoplasm, as we described it in the foregoing pages.

Utrecht, Oct. 1923.

stained black by the BIELSCHOWSKY-method, are always lying in a *vacuolated* part of the protoplasm. The same is seen here, and perhaps this has brought different observers to the conclusion, that in the cornea even the finest nerve-threads are surrounded by a lymph-space. In our opinion this has nothing to do with a lymph-space, but it is simply a vacuolisation of that part of the protoplasm, in which the neurofibrillae are imbedded, a vacuolisation which perhaps has a physiological significance, being a factor of the conductivity of the nerve-threads, the faculty of conducting a nervous current possibly being confined to neurofibrillae imbedded in a more fluid protoplasmatic medium.

Morphologically this phenomenon of course may create the appearance, that the nervous fibrillae are lying besides the protoplasm of the connective-tissue cells and of their processes. But a careful study of our preparations always convinced us again that this is

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Mathematics. — “*On the Product and Summability of Infinite Series.* By Dr. M. J. BELINFANTE. (Communicated by Prof. L. E. J. BROUWER).

(Communicated at the meeting of May 26, 1923).

In a previous article entitled “A Generalisation of MERTENS’ Theorem” we have proved the following theorem¹⁾:

Theorem 1. The product of a series which is joinable of order p and a series which is summable of order q is summable of order $p + q$.

We now will prove that this theorem is also valid, if p and q are no longer integers (§ 1). We further remark that theorem 1 contains as a special case the following theorem of ROSENBLATT²⁾:

Theorem 1a. If $\sum a_n$ and $\sum b_n$ are joinable of order p and q , their product is summable of order $p + q$.

ROSENBLATT discovered his theorem by generalising the following theorem of HARDY³⁾:

Theorem 2. If $\sum a_n$ and $\sum b_n$ are convergent and satisfy the relations $|na_n| < \kappa$ and $|nb_n| < \kappa$, then the product is also convergent.

Thus we are led to the question: is it also allowed to remove one of the conditions $|na_n| < \kappa$, $|nb_n| < \kappa$?

We will prove by an example that the answer must be negative, and by another example we will prove that the conditions $|na_n| < \kappa$ and $|nb_n| < \kappa$ together with the convergence of $\sum a_n$ and $\sum b_n$ do not necessarily imply the condition $|nc_n| < \kappa'$. ($\sum c_n$ is the product-series of $\sum a_n$ and $\sum b_n$).

Hence we have a priori no right to state the following extension of theorem 2:

¹⁾ Proceedings, Vol. XXVI, (p. 203—215). The article will be referred to as “Art. Mert”.

²⁾ Art. Mert., p. 214, 215.

³⁾ Jahrbuch über die Fortschritte der Mathematik, Bd. 44, p. 284, 1913.

Theorem 3. *If the series $\Sigma a_n^{(1)}, \Sigma a_n^{(2)}, \dots, \Sigma a_n^{(k)}$ are convergent and satisfy the conditions $|na_n^{(i)}| < x$ whatever be n and i , then the product of these k series is also convergent.*

A proof of this theorem will be given in § 2. In § 3 we define "summability of infinite order" and we prove a theorem concerning it.

§ 1.

The mean-values of order p of the series $a_1 + a_2 + \dots$ are now defined by the following expression:

$$\frac{S_n^{(p+1)}}{A_n^{(p+1)}}$$

where

$$A_n^{(k)} = \frac{\Gamma(n+k-1)}{\Gamma(n) \cdot \Gamma(k)}; A_n^{(0)} = 0; A_1^{(0)} = 1 \quad \dots \quad (1)$$

$$S_n^{(k)} = a_1 A_n^{(k)} + a_2 A_{n-1}^{(k)} + \dots + a_n A_1^{(k)} \quad \dots \quad (2)$$

If p is an integer, these definitions correspond with the definitions of our previous article. Our proof of theorem 1 for integral values of p and q was wholly based on the following theorem:

Theorem 4. *If Σa_n is summable of order p , then Σa_n is also summable of order $p+1$.*

and on the following relations:

$$\begin{aligned} S_1^{(p)} T_n^{(q)} + S_2^{(p)} T_{n-1}^{(q)} + \dots + S_n^{(p)} T_1^{(q)} &= \\ &= S_1^{(p-1)} T_n^{(q+1)} + S_2^{(p-1)} T_{n-1}^{(q+1)} + \dots + S_n^{(p-1)} T_1^{(q+1)} \end{aligned} \quad (3)$$

$$W_n^{(p+q)} = S_1^{(p)} T_n^{(q)} + S_2^{(p)} T_{n-1}^{(q)} + \dots + S_n^{(p)} T_1^{(q)} \quad \dots \quad (4)$$

$$A_n^{(p+q)} = A_1^{(p)} A_n^{(q)} + A_2^{(p)} A_{n-1}^{(q)} + \dots + A_n^{(p)} A_1^{(q)} \quad \dots \quad (5)$$

$$A_{i+1}^{(p)} \geq A_i^{(p)} \quad \text{if} \quad p > 1 \quad \dots \quad (6)$$

$$\lim_{n=\infty} A_n^{(p+1)} = \infty \quad \text{if} \quad p > 0 \quad \dots \quad (7)$$

$$\lim_{n \rightarrow \infty} \frac{A_n^{(p+1)}}{A_n^{(p+q+1)}} = 0 \quad (8)$$

Otherwise no use is made of the fact that p and q were integers. Therefore, since CHAPMAN¹⁾ has proved that theorem 4 remains valid if p is no longer an integer, we have only to prove that the relations (3)—(8) also exist if p and q are no integers, and our original proof (which consisted of three parts²⁾) remains valid.

Now the formula's (3) and (5) are an immediate consequence of the relations:

$$A_n^{(p+1)} = A_1^{(p)} + A_2^{(p)} + \dots + A_n^{(p)} \quad (A)$$

$$S_n^{(p+1)} = S_1^{(p)} + S_2^{(p)} + \dots + S_n^{(p)} \quad (B)$$

as follows from our previous article³⁾.

Hence it is sufficient to prove that the relations (A), (B), (4), (6), (7) and (8) are true if $p > 0$ and $q > 0$.

Proof of (A).

$$\begin{aligned} A_1^{(p)} + A_2^{(p)} + \dots + A_n^{(p)} &= \frac{\Gamma(p)}{\Gamma(1) \cdot \Gamma(p)} + \frac{\Gamma(p+1)}{\Gamma(2) \cdot \Gamma(p)} + \dots + \frac{\Gamma(p+n-1)}{\Gamma(n) \cdot \Gamma(p)} \\ &= \frac{1}{\Gamma(p)} \cdot \left[\frac{\Gamma(p)}{\Gamma(1)} + \frac{\Gamma(p+1)}{\Gamma(2)} + \dots + \frac{\Gamma(p+n-1)}{\Gamma(n)} \right] \\ A_n^{(p+1)} &= \frac{\Gamma(p+n)}{\Gamma(n) \cdot \Gamma(p+1)} = \frac{1}{\Gamma(p)} \cdot \frac{\Gamma(p+n)}{p \cdot \Gamma(n)} \end{aligned}$$

Hence it is sufficient to prove:

$$\frac{\Gamma(p+n)}{p \cdot \Gamma(n)} = \frac{\Gamma(p)}{\Gamma(1)} + \frac{\Gamma(p+1)}{\Gamma(2)} + \dots + \frac{\Gamma(p+n-1)}{\Gamma(n)} \quad (9)$$

This may be proved by induction: (9) is satisfied if $n=1$, and adding $\frac{\Gamma(p+n)}{\Gamma(n+1)} = \frac{\Gamma(p+n)}{n \cdot \Gamma(n)}$ to each member of (9) we have:

¹⁾ Proc. of the Lond. Math. Soc., Ser. 2 Vol 9 p. 369—409.

²⁾ Art. Mert. p. 204—211.

³⁾ Art. Mert. p. 204.

$$\frac{\Gamma(p+n)}{\Gamma(n)} \cdot \left[\frac{1}{p} + \frac{1}{n} \right] = \frac{\Gamma(p)}{\Gamma(1)} + \frac{\Gamma(p+1)}{\Gamma(2)} + \dots + \frac{\Gamma(p+n)}{\Gamma(n+1)}$$

or :

$$\frac{(p+n) \cdot \Gamma(p+n)}{pn \cdot \Gamma(n)} = \frac{\Gamma(p)}{\Gamma(1)} + \frac{\Gamma(p+1)}{\Gamma(2)} + \dots + \frac{\Gamma(p+n)}{\Gamma(n+1)}$$

$$\frac{\Gamma(p+n+1)}{p \cdot \Gamma(n+1)} = \frac{\Gamma(p)}{\Gamma(1)} + \frac{\Gamma(p+1)}{\Gamma(2)} + \dots + \frac{\Gamma(p+n)}{\Gamma(n+1)}$$

Proof of (B).

$$\begin{aligned} S_1^{(p)} + S_2^{(p)} + \dots + S_n^{(p)} &= \\ &= a_1 A_1^{(p)} + [a_1 A_2^{(p)} + a_2 A_1^{(p)}] + \dots + [a_1 A_n^{(p)} + a_2 A_{n-1}^{(p)} + \dots + a_n A_1^{(p)}] \\ &= a_1 [A_1^{(p)} + A_2^{(p)} + \dots + A_n^{(p)}] + a_2 [A_1^{(p)} + \dots + A_{n-1}^{(p)}] + \dots + a_n A_1^{(p)} \end{aligned}$$

Therefore, with the aid of (A):

$$S_1^{(p)} + S_2^{(p)} + \dots + S_n^{(p)} = a_1 A_n^{(p+1)} + a_2 A_{n-1}^{(p+1)} + \dots + a_n A_1^{(p+1)} = S_n^{(p+1)}$$

Proof of (4).

$$\begin{aligned} W_n^{(p+q)} &= c_1 A_n^{(p+q)} + c_2 A_{n-1}^{(p+q)} + \dots + c_n A_1^{(p+q)} \\ &= a_1 b_1 A_n^{(p+q)} + (a_1 b_2 + a_2 b_1) A_{n-1}^{(p+q)} + \dots + (a_1 b_n + a_2 b_{n-1} + \dots + a_n b_1) A_1^{(p+q)} \\ &= a_1 [b_1 A_n^{(p+q)} + b_2 A_{n-1}^{(p+q)} + \dots + b_n A_1^{(p+q)}] + \\ &\quad + a_2 [b_1 A_{n-1}^{(p+q)} + \dots + b_{n-1} A_1^{(p+q)}] + \dots + a_n [b_1 A_1^{(p+q)}] \\ &= a_1 T_n^{(p+q)} + a_2 T_{n-1}^{(p+q)} + \dots + a_n T_1^{(p+q)} \\ &= s_1 T_n^{(p+q)} + (s_2 - s_1) T_{n-1}^{(p+q)} + \dots + (s_n - s_{n-1}) T_1^{(p+q)} \\ &= s_1 [T_n^{(p+q)} - T_{n-1}^{(p+q)}] + s_2 [T_{n-1}^{(p+q)} - T_{n-2}^{(p+q)}] + \dots + s_n T_1^{(p+q)} \\ &= S_1^{(1)} T_n^{(p+q-1)} + S_2^{(1)} T_{n-1}^{(p+q-1)} + \dots + S_n^{(1)} T_1^{(p+q-1)} \\ &= S_1^{(p)} T_n^{(q)} + S_2^{(p)} T_{n-1}^{(q)} + \dots + S_n^{(p)} T_1^{(q)}. \end{aligned}$$

Proof of (6).

We have to prove:

$$A_{i+1}^{(p)} \geq A_i^{(p)} \quad \text{if} \quad p > 1$$

or:

$$\begin{aligned} \frac{\Gamma(p+i)}{\Gamma(i+1) \cdot \Gamma(p)} &\geq \frac{\Gamma(p+i-1)}{\Gamma(i) \cdot \Gamma(p)} \\ \frac{(p+i-1) \cdot \Gamma(p+i-1)}{i \cdot \Gamma(i) \cdot \Gamma(p)} &\geq \frac{\Gamma(p+i-1)}{\Gamma(i) \cdot \Gamma(p)} \\ \frac{p+i-1}{i} &\geq 1, \text{ which follows from } p > 1. \end{aligned}$$

Proof of (7).

$$\begin{aligned} A_n^{(p+1)} &= \frac{\Gamma(n+p)}{\Gamma(n) \cdot \Gamma(p+1)} = \frac{(n+p-1) \cdot (n+p-2) \dots (p+1) \cdot \Gamma(p+1)}{(n-1) \cdot (n-2) \dots 1 \cdot \Gamma(p+1)} \\ &= \left(1 + \frac{p}{n-1}\right) \cdot \left(1 + \frac{p}{n-2}\right) \dots \left(1 + \frac{p}{1}\right) > 1 + p \left(1 + \frac{1}{2} + \dots + \frac{1}{n-1}\right) \end{aligned}$$

Hence $\lim_{n \rightarrow \infty} A_n^{(p+1)} = \infty$ if $p > 0$.

Proof of (8).

$$\begin{aligned} \frac{A_n^{(p+1)}}{A_n^{(p+q+1)}} &= \frac{\Gamma(n+p)}{\Gamma(n) \cdot \Gamma(p+1)} \times \frac{\Gamma(n) \cdot \Gamma(p+q+1)}{\Gamma(n+p+q)} \\ &= \frac{\Gamma(n+p)}{\Gamma(n+p+q)} \times \frac{\Gamma(p+q+1)}{\Gamma(p+1)} \end{aligned} \quad (10)$$

Since $\lim_{n \rightarrow \infty} \frac{\Gamma(n+a)}{\Gamma(n)} = \lim_{n \rightarrow \infty} \Gamma(a+1) \cdot A_n^{(a+1)} = \infty$, if $a > 0$, we have:

$\lim_{n \rightarrow \infty} \frac{\Gamma(n+p)}{\Gamma(n+p+q)} = 0$, if $q > 0$. Hence we have from (10):

$$\lim_{n \rightarrow \infty} \frac{A_n^{(p+1)}}{A_n^{(p+q+1)}} = 0 \quad \text{if} \quad q > 0.$$

§ 2.

That the condition $|na_n| < \varepsilon$, or even $\lim_{n \rightarrow \infty} na_n = 0$ is not sufficient

to secure the convergence of the product of the convergent series $a_1 + a_2 + \dots$ and another convergent series $b_1 + b_2 + \dots$ may be seen from the following example:

The series

$$\frac{1}{2 \log 2} - \frac{1}{3 \log 3} + \frac{1}{4 \log 4} - \dots$$

is convergent and satisfies the condition $\lim_{n \rightarrow \infty} n a_n = 0$; the product with the convergent series

$$\frac{1}{\log \log 2} - \frac{1}{\log \log 3} + \frac{1}{\log \log 4} - \dots$$

is the series:

$$\begin{aligned} & \frac{1}{2 \log 2} \cdot \frac{1}{\log \log 2} - \left[\frac{1}{3 \log 3} \cdot \frac{1}{\log \log 2} + \frac{1}{2 \log 2} \cdot \frac{1}{\log \log 3} \right] + \\ & + \left[\frac{1}{4 \log 4} \cdot \frac{1}{\log \log 2} + \frac{1}{3 \log 3} \cdot \frac{1}{\log \log 3} + \frac{1}{2 \log 2} \cdot \frac{1}{\log \log 4} \right] - \dots \end{aligned}$$

which does *not* converge, since the absolute value of the general term u_{n-1} is:

$$\frac{1}{n \log n} \cdot \frac{1}{\log \log 2} + \frac{1}{(n-1) \log (n-1)} \cdot \frac{1}{\log \log 3} + \dots + \frac{1}{2 \log 2} \cdot \frac{1}{\log \log n}$$

which is greater than:

$$\frac{1}{\log \log n} \left[\frac{1}{n \log n} + \frac{1}{(n-1) \log (n-1)} + \dots + \frac{1}{2 \log 2} \right] > \frac{\log \log (n+1) - \log \log 2}{\log \log n}$$

as follows easily from: $\frac{1}{p \log p} > \int_p^{p+1} \frac{dx}{x \log x}$.

Hence u_n remains > 1 , if n is sufficiently great.

That the conditions $|n a_n| < \kappa$ and $|n b_n| < \kappa$ do not imply $|n c_n| < \kappa$ if the series Σa_n and Σb_n are convergent, is seen by the following example:

The series:

$$\log 2 = 1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots$$

converges and satisfies the condition $|n a_n| \leq 1$. The square of this series is:

$$1 - \left(1 \cdot \frac{1}{2} + \frac{1}{2} \cdot 1 \right) + \left(1 \cdot \frac{1}{3} + \frac{1}{2} \cdot \frac{1}{2} + \frac{1}{3} \cdot 1 \right) - \left(1 \cdot \frac{1}{4} + \frac{1}{2} \cdot \frac{1}{3} + \frac{1}{3} \cdot \frac{1}{2} + \frac{1}{4} \cdot 1 \right) + \dots$$

or, with the aid of the identity ¹⁾:

$$1 \cdot \frac{1}{n-1} + \frac{1}{2} \cdot \frac{1}{n-2} + \frac{1}{3} \cdot \frac{1}{n-3} + \dots + \frac{1}{n-1} \cdot 1 = \frac{2}{n} \cdot \left(1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n-1} \right)$$

this becomes

$$\frac{2}{2} - \frac{2}{3} \cdot \left(1 + \frac{1}{2} \right) + \frac{2}{4} \cdot \left(1 + \frac{1}{2} + \frac{1}{3} \right) - \frac{2}{5} \cdot \left(1 + \frac{1}{2} + \frac{1}{3} + \frac{1}{4} \right) + \dots$$

Hence:

$$n |c_n| = n \cdot \frac{2}{n+1} \cdot \left(1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n} \right)$$

$$\lim_{n \rightarrow \infty} n |c_n| = 2 \cdot \lim_{n \rightarrow \infty} \left(1 + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n} \right) = \infty.$$

Proof of theorem 3.

We denote the n^{th} term of the product of the series

$$\Sigma a_n^{(i)}, \Sigma a_n^{(j)}, \Sigma a_n^{(k)}, \dots$$

by $a_n^{(i,j,k,\dots)}$, and the sum of the first n terms of the same product by $A_n^{(i,j,k,\dots)}$. Hence:

$$A_n^{(i,j,k,\dots)} = a_1^{(i,j,k,\dots)} + a_2^{(i,j,k,\dots)} + \dots + a_n^{(i,j,k,\dots)}$$

Further we define:

$$^{(p,q,r,\dots)} a_n = n \cdot a_n^{(p,q,r,\dots)}$$

$$\begin{aligned} ^{(p,q,r,\dots)} a_n^{(i,k,l,\dots)} &= \\ &= a_1^{(p,q,r,\dots)} a_n^{(i,k,l,\dots)} + 2a_2^{(p,q,r,\dots)} a_{n-1}^{(i,k,l,\dots)} + \dots + na_n^{(p,q,r,\dots)} a_1^{(i,k,l,\dots)} \\ ^{(p,q,r,\dots)} A_n &= ^{(p,q,r,\dots)} a_1 + ^{(p,q,r,\dots)} a_2 + \dots + ^{(p,q,r,\dots)} a_n \\ &= a_1^{(p,q,r,\dots)} + 2a_2^{(p,q,r,\dots)} + \dots + na_n^{(p,q,r,\dots)} \\ ^{(p,q,r,\dots)} A_n^{(i,k,l,\dots)} &= ^{(p,q,r,\dots)} a_1^{(i,k,l,\dots)} + ^{(p,q,r,\dots)} a_2^{(i,k,l,\dots)} + \dots + ^{(p,q,r,\dots)} a_n^{(i,k,l,\dots)} \end{aligned}$$

We now prove the following relation:

¹⁾ This identity can be proved by equating the coefficients of x^n in both members of:

$$\begin{aligned} \int_0^x \frac{2 \log(1+x)}{1+x} \cdot dx &= \int_0^x 2 \left(x - \frac{x^2}{2} + \frac{x^3}{3} \dots \right) \cdot (1 - x + x^2 - \dots) dx = \\ &= \left(x - \frac{x^2}{2} + \frac{x^3}{3} \dots \right)^2 = [\log(1+x)]^2 \end{aligned}$$

$${}^{(1,2,\dots,k)}A_n = \sum_{i_1 \dots i_k} {}^{(i_1)}A_n^{(i_2, i_3, \dots, i_k)} - (k-1) \cdot A_n^{(1, 2, \dots, k)} \quad (1)$$

We introduce the following power-series:

$$\varphi_k(x) = \sum_1^{\infty} a_n^{(k)} x^n$$

$$\varphi_{p,q,r,\dots}(x) = \varphi_p(x) \cdot \varphi_q(x) \cdot \varphi_r(x) \dots$$

It is easy to verify that the following assertions are immediate consequences of the foregoing definitions:

$$a_n^{(i_1, i_2, \dots, i_r)} \text{ is the coefficient of } x^n \text{ in } \frac{\varphi_{i_1, i_2, \dots, i_r}}{x^{r-1}}$$

$${}^{(i_1, i_2, \dots, i_r)}a_n \text{ is the coefficient of } x^{n-1} \text{ in } \frac{d}{dx} \frac{\varphi_{i_1, i_2, \dots, i_r}}{x^{r-1}}$$

$${}^{(i_1, i_2, \dots, i_r)}a_n {}^{(i_{r+1}, i_{r+2}, \dots, i_{r+p})} \text{ is the coefficient of } x^n \text{ in:}$$

$$\frac{\varphi_{i_{r+1}, i_{r+2}, \dots, i_{r+p}}}{x^{p-1}} \cdot \frac{d}{dx} \frac{\varphi_{i_1, i_2, \dots, i_r}}{x^{r-1}}$$

Now we have:

$$\frac{d}{dx} \frac{\varphi_{1, 2, \dots, k}}{x^{k-1}} = \frac{1}{x^{k-1}} \cdot \frac{d}{dx} \varphi_{1, 2, \dots, k} - (k-1) \cdot \frac{\varphi_{1, 2, \dots, k}}{x^k}$$

or, since $\varphi_{1, 2, \dots, k} = \varphi_1 \cdot \varphi_2 \dots \varphi_k$ and hence

$$\frac{d}{dx} \varphi_{1, 2, \dots, k} = \sum_{i_1 \dots i_k} \varphi_{i_2, i_3, \dots, i_k} \cdot \frac{d\varphi_{i_1}}{dx},$$

$$\frac{d}{dx} \frac{\varphi_{1, 2, \dots, k}}{x^{k-1}} = \frac{1}{x} \cdot \sum \frac{\varphi_{i_2, i_3, \dots, i_k}}{x^{k-2}} \cdot \frac{d\varphi_{i_1}}{dx} - \frac{k-1}{x} \cdot \frac{\varphi_{1, 2, \dots, k}}{x^{k-1}}.$$

Equating the coefficients of x^{m-1} in both members we get:

$${}^{(1, 2, \dots, k)}a_m = \sum_{(i)} {}^{(i_1)}a_m^{(i_2, i_3, \dots, i_k)} - (k-1) \cdot a_m^{(1, 2, \dots, k)}$$

Substitution of $m = 1, 2, \dots, n$ and addition of the results gives

$${}^{(1, 2, \dots, k)}A_n = \sum_{(i)} {}^{(i_1)}A_n^{(i_2, i_3, \dots, i_k)} - (k-1) \cdot A_n^{(1, 2, \dots, k)} \quad (1)$$

Our proof of theorem 3 is based on the following theorem:

If Σu_n is summable, then Σu_n is convergent provided:

$$\lim_{n \rightarrow \infty} \frac{1}{n} (u_1 + 2u_2 + \dots + nu_n) = 0.$$

This follows from TAUBER's theorem by the remark that the function $\Sigma a_n x^n$ has a limit as $x \rightarrow 1$, if Σa_n is summable. (See our article: "On a Generalisation of TAUBER's theorem concerning Power series". These Proceedings XXVI, p. 224).

Now let $\Sigma a_n^{(1)}, \Sigma a_n^{(2)}, \dots, \Sigma a_n^{(k)}$ be convergent series whose terms satisfy the condition $|na_n^{(i)}| < \kappa$ whatever be i and n . Since the product-series is certainly summable of order k , we have only to prove:

$$\lim_{n=\infty} \frac{1}{n} [a_1^{(1,2,\dots,k)} + 2a_2^{(1,2,\dots,k)} + \dots + na_n^{(1,2,\dots,k)}] = 0$$

or:

$$\lim_{n=\infty} \frac{1}{n} A_n^{(1,2,\dots,k)} = 0$$

Hence we see by (1) that it is sufficient to prove the following relations:

$$\lim_{n=\infty} \frac{A_n^{(1,2,\dots,k)}}{n} = 0 \quad (2)$$

$$\lim_{n=\infty} \frac{1}{n} A_n^{(i_1, i_2, \dots, i_k)} = 0 \quad (3)$$

Proof of (2).

We prove by induction the inequality:

$$|A_n^{(1,2,\dots,k)}| < \kappa^k [\log(n+1) + C]^k$$

where C is EULER's constant. Indeed we have:

$$|A_n^{(1)}| = |a_1^{(1)} + a_2^{(1)} + \dots + a_n^{(1)}| \leq \kappa \left(1 + \frac{1}{2} + \dots + \frac{1}{n}\right) < \kappa [\log(n+1) + C]$$

and from

$$|A_n^{(1,2,\dots,i)}| < \kappa^i [\log(n+1) + C]^i$$

we deduce:

$$\begin{aligned} |A_n^{(1,2,\dots,i,i+1)}| &= |a_1^{(i+1)} A_n^{(1,2,\dots,i)} + a_2^{(i+1)} A_{n-1}^{(1,2,\dots,i)} + \dots + a_n^{(i+1)} A_1^{(1,2,\dots,i)}| \\ &< \kappa^i [\log(n+1) + C]^i [|a_1^{(i+1)}| + |a_2^{(i+1)}| + \dots + |a_n^{(i+1)}|] \\ &< \kappa^{i+1} [\log(n+1) + C]^i \left[1 + \frac{1}{2} + \dots + \frac{1}{n}\right] \\ &< \kappa^{i+1} [\log(n+1) + C]^{i+1} \end{aligned}$$

Since $\lim_{n \rightarrow \infty} \frac{[\log(n+1) + C]^k}{n} = 0$, it follows that:

$$\lim_{n \rightarrow \infty} \frac{A_n^{(1, 3, \dots, k)}}{n} = 0$$

Proof of (3).

We prove that the relation (3) is true for $k = p$, provided that our theorem 3 is true for $k = p-1$. Hence it follows that if the theorem is true for $k = p-1$, it is also true for $k = p$, and since HARDY has shown that it is certainly true for $k = 2$, our theorem will be proved.

From the hypothesis that theorem 3 is true for $k = p-1$, it follows that: $\lim_{n \rightarrow \infty} A_n^{(i_1, i_2, \dots, i_{p-1})} = s_{i_1} \cdot s_{i_2} \dots s_{i_{p-1}} = s$, if the series $\sum a_n^{(i_1)}, \sum a_n^{(i_2)}, \dots, \sum a_n^{(i_{p-1})}$ converge respectively to $s_{i_1}, s_{i_2}, \dots, s_{i_{p-1}}$.

Indeed $A_n^{(i_1, i_2, \dots, i_{p-1})}$ is by definition the sum of the first n terms of the product:

$$[\sum a_n^{(i_1)}] \cdot [\sum a_n^{(i_2)}] \dots [\sum a_n^{(i_{p-1})}]$$

Now we have:

$$^{(i_p)} a_n^{(i_1, i_2, \dots, i_{p-1})} = a_1^{(i_p)} \cdot a_m^{(i_1, \dots, i_{p-1})} + 2a_2^{(i_p)} \cdot a_{m-1}^{(i_1, \dots, i_{p-1})} + \dots + m a_m^{(i_p)} \cdot a_1^{(i_1, \dots, i_{p-1})}$$

Substitution of $m = 1, 2, \dots, n$ and addition gives:

$$^{(i_p)} A_n^{(i_1, i_2, \dots, i_{p-1})} = a_1^{(i_p)} \cdot A_n^{(i_1, \dots, i_{p-1})} + 2a_2^{(i_p)} \cdot A_{n-1}^{(i_1, \dots, i_{p-1})} + \dots + n a_n^{(i_p)} \cdot A_1^{(i_1, \dots, i_{p-1})}$$

Put $A_r^{(i_1, i_2, \dots, i_{p-1})} = s + h_r$, then we have $\lim_{n \rightarrow \infty} h_n = 0$, and:

$$\begin{aligned} ^{(i_p)} A_n^{(i_1, i_2, \dots, i_{p-1})} &= s[a_1^{(i_p)} + 2a_2^{(i_p)} + \dots + n a_n^{(i_p)}] + \\ &\quad + [a_1^{(i_p)} h_n + 2a_2^{(i_p)} h_{n-1} + \dots + n a_n^{(i_p)} h_1] \\ &= P + Q. \end{aligned}$$

Since $a_1^{(i_p)} + a_2^{(i_p)} + \dots$ is convergent, we have by TAUBER's theorem

$$\lim_{n \rightarrow \infty} \frac{a_1^{(i_p)} + 2a_2^{(i_p)} + \dots + n a_n^{(i_p)}}{n} = 0$$

hence $\lim_{n \rightarrow \infty} \frac{P}{n} = 0$.

Substituting the inequality $n |a_n^{(i_p)}| < \varkappa$ in Q , we have

$$|Q| < \varkappa \cdot (|h_1| + |h_2| + \dots + |h_n|)$$

Since $\lim_{n \rightarrow \infty} h_n = 0$, we also have $\lim_{n \rightarrow \infty} \frac{|h_1| + \dots + |h_n|}{n} = 0$, hence

$$\lim_{n \rightarrow \infty} \frac{Q}{n} = 0.$$

Therefore:

$$\lim_{n \rightarrow \infty} \frac{{}^{(i_p)}A_n^{(i_1, i_2, \dots, i_{p-1})}}{n} = \lim_{n \rightarrow \infty} \frac{P}{n} + \lim_{n \rightarrow \infty} \frac{Q}{n} = 0.$$

§ 3.

Definition 1). If the expression $\frac{S_n^{(p)}}{A_n^{(p)}}$ tends to a limit as n and p are both increasing to ∞ with the restriction that $\lim_{n \rightarrow \infty} \frac{p}{n} = 0$, then we say that the series $a_1 + a_2 + \dots$ is summable of infinite order.

Theorem 5. If a series is summable of some finite order, it is also summable of infinite order and has the same sum.

Proof. We have by hypothesis $\lim_{n \rightarrow \infty} \frac{S_n^{(k)}}{A_n^{(k)}} = s$. Put $\frac{S_r^{(k)}}{A_r^{(k)}} = s + h_r$, then $\lim_{n \rightarrow \infty} h_n = 0$.

$$\begin{aligned} S_n^{(p)} &= S_1^{(k)} A_n^{(p-k)} + S_2^{(k)} A_{n-1}^{(p-k)} + \dots + S_n^{(k)} A_1^{(p-k)} \\ &= s[A_1^{(k)} A_n^{(p-k)} + A_2^{(k)} A_{n-1}^{(p-k)} + \dots + A_n^{(k)} A_1^{(p-k)}] + \\ &\quad + [h_1 A_1^{(k)} A_n^{(p-k)} + h_2 A_2^{(k)} A_{n-1}^{(p-k)} + \dots + h_n A_n^{(k)} A_1^{(p-k)}] \\ &= s \cdot A_n^{(p)} + R. \end{aligned}$$

We have for every r between 1 and n :

$$\begin{aligned} R &= [h_1 A_1^{(k)} A_n^{(p-k)} + \dots + h_r A_r^{(k)} A_{n-r+1}^{(p-k)}] + [h_{r+1} A_{r+1}^{(k)} A_{n-r}^{(p-k)} + \dots + \\ &\quad + h_n A_n^{(k)} A_1^{(p-k)}] \\ &= P + Q \end{aligned}$$

1) The notation is the same as in § 1.

Now whatever be $\varepsilon > 0$, it is possible to find r so that $|h_{r+i}| < \varepsilon$; further let h be chosen so that $|h_i| < h$ whatever be i , then we have if $n > r$:

$$|P| < h \cdot A_n^{(p-k)} A_r^{(k+1)} ; \quad |Q| < \varepsilon A_n^{(p)}$$

$$\lim_{n \rightarrow \infty} \frac{|P|}{A_n^{(p)}} = 0, \text{ since:}$$

$$\begin{aligned} \frac{A_n^{(p-k)}}{A_n^{(p)}} &= \frac{\Gamma(n+p-k-1)}{\Gamma(n) \cdot \Gamma(p-k)} \cdot \frac{\Gamma(n) \cdot \Gamma(p)}{\Gamma(n+p-1)} = \frac{\Gamma(n+p-k-1)}{\Gamma(n+p-1)} \cdot \frac{\Gamma(p)}{\Gamma(p-k)} \\ &= \frac{\Gamma(n+p-k-1)}{(n+p-2)(n+p-3)\dots(n+p-k-1) \cdot \Gamma(n+p-k-1)} \\ &\quad \cdot \frac{(p-1)(p-2)\dots(p-k) \cdot \Gamma(p-k)}{\Gamma(p-k)} \\ &= \frac{p-1}{(n-1)+(p-1)} \cdot \frac{p-2}{(n-1)+(p-2)} \dots \frac{p-k}{(n-1)+(p-k)} \\ &< \frac{p}{n-1+p-1} < \frac{p}{n} \text{ and } \lim_{n \rightarrow \infty} \frac{p}{n} = 0. \end{aligned}$$

$$\frac{|Q|}{A_n^{(p)}} < \varepsilon. \text{ Since } \varepsilon > 0 \text{ is arbitrary, it follows that:}$$

$$\lim_{n \rightarrow \infty} \frac{Q}{A_n^{(p)}} = 0. \text{ Therefore:}$$

$$\lim_{n \rightarrow \infty} \frac{S_n^{(p)}}{A_n^{(p)}} = s + \lim_{n \rightarrow \infty} \frac{R}{A_n^{(p)}} = s + \lim_{n \rightarrow \infty} \frac{P}{A_n^{(p)}} + \lim_{n \rightarrow \infty} \frac{Q}{A_n^{(p)}} = s.$$

Note 1.

Concerning the question whether a series may be summable of infinite order without being summable of any finite order, we add the following remark:

Suppose we have a series with real terms; let the mean-values of order p oscillate between the limits m_p and M_p , then we have the following inequality:

$$m_p \leq m_{p+1} \leq M_{p+1} \leq M_p.$$

Now suppose it were possible to construct a series so that:

$$m_p \neq m_{p+1}; M_p \neq M_{p+1}; \lim_{p \rightarrow \infty} m_p = \lim_{p \rightarrow \infty} M_p = \mu;$$

then it is easy to prove that such a series would be summable of infinite order, but *not* of some finite order. But a series of this kind *cannot exist*; this may be proved as follows:

W. GROSS¹⁾ has proved that the values of

$$\varphi_0(x) = a_1 x + a_2 x^2 + \dots$$

lie between m_p and M_p provided $1-x$ is less than a certain positive quantity. Hence $\lim. m_p = \lim. M_p = \mu$ implies $\lim_{x \rightarrow 1} \varphi_0(x) = \mu$. Therefore, since the mean-values of Σa_n are limited, we have by a theorem of LITTLEWOOD²⁾ that Σa_n is summable of finite order, which is contradictory to the hypothesis.

In order to find a series that is summable of infinite order, without being summable of some finite order, we might try to construct a series with mean-values which oscillate about an infinite interval.

I have not succeeded in constructing such a series, nor have I been able to prove that such a series cannot exist.

Note 2.

After this article was written, my attention was drawn to the article "Contributions to the Arithmetic Theory of Series" by G. H. HARDY and J. E. LITTLEWOOD³⁾. This article contains a proof of theorem 3 of the present paper which is totally different from the one given above.⁴⁾ The same article also contains a generalisation of MERTENS' theorem, which I gave in my previous article⁵⁾.

¹⁾ Sitzungsberichte der Kaiserl. Akad. der Wissensch. in Wien Abt. II^a 124 p. 1017—1037; 1915.

²⁾ See for instance our article "On Power-Series of the form $x^{p_0} - x^{p_1} + x^{p_2} - \dots$ " These Proceedings, Vol. XXVI, p. 457.

³⁾ Proc. of the Lond. Math. Soc., Ser. 2, Vol. 11, p. 411—478.

⁴⁾ Loc. cit. p. 464.

⁵⁾ Art. Mert. p. 203; HARDY and LITTLEWOOD, l. c. p. 461.

Botany. — "*The first Carbohydrates that originate during the Assimilatory Process. A physiological Study with Variegated Leaves*". By Prof. TH. WEEVERS. (Communicated by Prof. J. W. MOLL).

(Communicated at the meeting of November 24, 1923).

Like the inquiry described in a previous communication¹⁾ the present investigation was undertaken with variegated plants by using a kind of differentiation method. Of different species metabolic processes were compared in green and in variegated parts of one and the same specimen. The green parts being autotropic, and the variegated parts depending for their nutrition on the green ones, differences arise, the study of which might increase our knowledge of plant-metabolism. In this paper I propose to discuss the problem of the first carbohydrates that originate during assimilation.

Introduction and a review of the literature.

Although since the work of J. SACHS starch has sometimes been called the first visible product of carbon-assimilation, it may nonetheless be considered rather as the last link of a chain of chemical processes in the chloroplast. This view is supported by the fact observed by KRAUS²⁾ that Spirogyracells exhibit formation of oxygen almost directly when assimilation commences, whereas formation of starch is noticeable only after some minutes.

Both SCHIMPER³⁾ and ARTHUR MEYER⁴⁾ pointed to the significance of the soluble carbohydrates. The former looked upon glucose not only as the product of hydrolysis of polyoses and bioses which did duty as matter of transport, but also as the substance that preceded the formation of the starch-molecule.

This view was generally received until in their publication on the assimilation of Tropaeolum BROWN and MORRIS⁵⁾ brought forward the hypothesis that saccharose is to be considered as the primary carbohydrate.

¹⁾ These Proceedings. Vol. XXVI, p. 755.

²⁾ KRAUS, Jahrb. f. Wiss. Bot. 1869.

³⁾ and ⁴⁾ SCHIMPER and A. MEYER, Bot. Zeitung 1885.

⁵⁾ BROWN and MORRIS, Journ. Chem. Soc. Trans. 1893.

WENT ¹⁾ sided with these authors as far as sugar-cane is concerned. Afterwards PARKIN ²⁾ has studied the snowdrop. In this subject the relations are simpler, as starch and maltose are virtually lacking, which was not the case in other subjects. This does away with most of the objections, rightly raised by A. J. KLUYVER ³⁾, to the method adopted by BROWN and MORRIS.

Indeed, considered narrowly, the results of BROWN and MORRIS's analyses do not, in my opinion, yield conclusive evidence for their conception that saccharose should be considered as the primary product.

PARKIN adheres to this conception in virtue of his observation that from above downward to the base of the leaf of the snowdrop the total amount of soluble carbohydrates augments, but that at the same time the saccharose decreases relatively to the monoses. The latter are then supposed to constitute the matter of transport to the bulb. PARKIN also thinks that the amount of monoses remains rather constant, and that on the other hand in the process of assimilation the saccharose increases in the day-time and decreases by night. If by day the transport from the leaf is inhibited, the increase of saccharose is still more considerable.

These observations, however, may also be due to the fact that the primary monoses when present in a certain quantity are converted into saccharose, and in respect of the difference in amount between the upper and the lower half of the green leaf, we attach a far greater importance to a comparison of the absolute values than to that of the relative ones. When calculating the absolute values from PARKIN's data it indeed appears that there is towards the base of the leaf a considerable increase of the monoses, but the saccharose alternately decreases and increases.

For this reason I think that the snowdrop has to be reinvestigated, all the more because CAMPBELL's ⁴⁾ inquiry with the beetroot clashes with PARKIN's view that saccharose should be considered as the primary product. CAMPBELL demonstrates by a series of analyses of leaves, picked every two hours, that when assimilation commences the monoses are the first to augment, then follows saccharose, at last starch. The maltose increases by night and is therefore generally looked upon as the product of starch hydrolysis.

It follows, then, that the question which is the primary product must still be considered as a moot point.

1) WENT, *Jahrb. f. Wiss. Bot.* 1898.

2) PARKIN, *Biochem. Journal* 1911.

3) A. J. KLUYVER, *Thesis Techn. University* 1914.

4) CAMPBELL, *Journ. f. agricultural Science* 1911/12.

Formerly it was believed that glucose was found almost in every plant, saccharose only in very few. Although the first may be correct, the second assertion is undoubtedly wrong as shall appear lower down. This hypothesis, therefore, cannot afford any ground for argumentation, which may more readily be derived from the logical reasoning that the simpler monoses will more likely be the primary product than saccharose.

It is also quite possible that not all plants behave in the same way. Just as well as one plant accumulates its carbohydrates in the form of sugars, the other in the form of inulin, the majority again in the form of starch, the primary product may also differ with these various behaviours.

It would seem to me that the comparison of the carbohydrates of green and variegated¹⁾ parts in one and the same specimen might throw some light upon this point.

In the chlorophyll-free parts the carbohydrates present can play the rôle of matter of transport or reserve material, but never that of primary assimilation product. As known, starch is lacking in yellow parts of variegated leaves; SACHS's iodine-test clearly marks the boundary between the chlorophyll-containing and the chlorophyll-free tissue. Excepted are only the cases in which the variegated leaves, contrary to the rule, possess chlorophyll-free stomata; then in the latter the starch-formation takes place in the leucoplasts as well as in the chloroplasts, that characterize the guard-cells of the majority of variegated leaves.²⁾

The question whether there is any difference between the soluble carbohydrates of the green and the variegated parts of the leaves, or between the green and the variegated shoots of one and the same plant has to my knowledge not yet been looked at.

Now it is quite possible that one and the same sugar performs different functions; viz., that it is the primary assimilation product in the green parts, and that it is reserve-material or matter of transport in the variegated parts. So there need not be any differences between the sugars of the variegated and those of the green parts, but if we do find them there is scope for conclusions.

BROWN and MORRIS (l.c.) asserted that glucose is used specially for the respiratory processes, while LINDET³⁾ maintains that fructose goes to the building up of the tissues. PARKIN and COLIN⁴⁾ arrived

¹⁾ By the term variegated we designate here the chlorophyll-free parts.

²⁾ KÜMMLER, *Jahrb. f. Wiss. Bot.* 1922.

³⁾ LINDET, *Bullet. Assoc. Chem. Sucr. T.* 28, 1909.

⁴⁾ COLIN, *Compt. Rendus. T.* 168, 1919.

at the same conclusion as BROWN and MORRIS, but a critical examination by DAVIS¹⁾ brought to light that the methods employed by the above-named observers for the differentiation of the two monoses were at fault. It is particularly for the quantitative polarimetrical determination of glucose and fructose in vegetable extracts that these methods offered some difficulties.

Method.

For the present I will, therefore, not attempt to differentiate glucose and fructose and will confine myself to monoses only. Our specific object, therefore, was to watch the occurrence of saccharose on the one side, and of monoses on the other. To this end the reduction of FEHLING's solution was estimated in one portion of the extract before, and in another portion after 24 hours' action of invertase (MERCK). The directly reducing sugars are not of necessity exclusively monoses, since maltose also reduces FEHLING directly. Although for the above-stated reasons maltose is not essential to our object, it had yet to be decided whether monoses occurred among the directly reducing sugars. To ascertain this a qualitative estimation with BARFOED's²⁾ reagent was made every time besides the quantitative determination with FEHLING. BARFOED's reagent: copper-acetate in a neutral or faintly acid solution, reacts with glucose and fructose, not with bioses.

In some cases we also applied the biochemical method of KLUYVER l.c. as *Torula monosa* ferments only monoses and by measuring the volume of the formed carbonic acid a quantitative determination is rendered possible. Our intention to form an estimate of the maltose by means of the differentiation method with *Torula dattila* and *Sacharomyces cerevisiae* (see KLUYVER l.c.), was abandoned.

The material was killed directly in boiling water, by which the invertase was destroyed; subsequently a just sufficient amount of basic lead-acetate solution was added to the aqueous extract, and the precipitate filtered off. One part of the filtrate was tested for monoses with BARFOED's reagent³⁾ after neutralization with acetic acid. To the remaining part of the filtrate disodium phosphate solution was added, and the lead-phosphate filtered off. Then the

¹⁾ DAVIS, Journ. Agric. Science. 1916.

²⁾ BARFOED, Zeitschr. f. anal. Chemie 1873. In spite of many attempts this method remained impracticable for a quantitative examination.

³⁾ The diluted solutions of fructose occurring in vegetable extracts are not precipitated by basic lead-acetate.

sugar-determination took place in the latter filtrate, after the iodometric method of SCHOORL¹⁾.

The leaves were plucked every time after a sunny day in September, the analysed quantity had as a rule a dry weight of ± 10 grams. The procentic values refer to dry weight.

Analytic research.

1. *Acer Negundo* L. fol. var. white-variegated. Full-grown green leaves and green parts of the variegated leaves.

1 to 2 % directly reducing sugars (monose-reaction +).

1 to 2 % saccharose, also starch²⁾.

Full-grown white leaves and parts of leaves, no monose or maltose.

1 to 2 % saccharose, no starch (except in the stomata).

Very young white parts of leaves.

1 %, directly reducing sugar, 1 % saccharose.

White leaf-stalks, 0,5 to 1 % saccharose, directly reducing sugars and starch only in traces, viz. at the base.

White branches (September) 0,1 % dir. reduc. sugar, saccharose 0,5 %, also starch.

When in the beginning of October the leaves begin to die off, the dir. reduc. sugar increases in the green parts, the saccharose diminishes (the first 2,5 %, the second 0,8 %), the variegated parts do not contain monoses. No more does the aurea variety of *Acer Negundo* contain monoses in the yellow parts.

2. *Ilex Aquifolium* L. fol. var.

Green: 1,2 % dir. reduc. sugar (monose-reaction +), 1,25 % saccharose.

White: no monose, nor maltose, 1 % saccharose.

3. *Hedera Helix* L. fol. var.

Green: 1 % dir. reduc. sugar (monose-reaction +), 2,5 % saccharose.

Variegated: no monose, nor maltose, 3 % saccharose.

4. *Humulus Lupulus* L. fol. var.

Green: 1,3 % dir. reduc. sugar (monose-reaction +), 2,4 % saccharose.

Variegated: no monose, nor maltose, saccharose 3 %.

5. *Euonymus japonica* Thb. fol. var.

Green: 0,9 % dir. reduc. sugar (monose-reaction +), 0,6 % saccharose.

Variegated: no monose, nor maltose, saccharose 0,5 %.

¹⁾ N. SCHOORL, Ned. Tijdschrift Pharmacie 1899. The influence, exerted by the saccharose present, on the reducing power of invert-sugar, was neglected.

²⁾ A glucosid is also contained in the leaves. It is soluble in water, cannot be hydrolyzed by emulsin, nor precipitated with basic lead acetate, and leaves after boiling with diluted HCl a brown resinous product (together with reducing sugar).

6. *Aesculus Hippocastanum* L. (specimen with variegated and green shoots).

Green: (midsummer-growth analysed in September) 3,4 % dir. reduc. sugar (monose-reaction +) 0,5 % saccharose.

Variegated: (midsummer-growth analysed in September) 1 % dir. reduc. sugar (monose-reaction +) 0,1 % saccharose.

7. *Cornus Sanguinea* L. fol. var.

Green 1,6 % dir. reduc. sugar (monose-reaction +) 2,8 % saccharose.

Variegated: 0,9 % dir. reduc. sugar (monose-reaction +) 3 % saccharose.

8. *Pelargonium zonale* Willd. White periclinal chimaera.

Green parts: 1 to 2 % dir. reduc. sugar (monose-reaction +), 1 à 2 % saccharose.

Variegated parts: no monose, nor maltose, 0,6 % saccharose.

When placing the plants in the dark ($t=10^{\circ}$ C.) the sugars disappear after 2×24 hours from the leaves, the starch likewise. The leaves still look normal then, they are not yellow. It is with these plants that we tried to ascertain which are the primary sugars in the initial assimilatory process.

After $\frac{1}{2}$ hours' insolation (per 10 grms dry weight) traces of dir. reduc. sugar, no saccharose.

After 1 hour's insolation 0,3 % dir. reduc. sugar traces of saccharose

After 3 hours' " 0,4 % " " " 0,3 % "

After 5 hours' " 0,6 % " " " 0,3 % "

9. *Aspidistra elatior*. Blume Sectorial variegated.

Green parts: 0,4 % dir. reduc. sugar (monose-reaction +), 0,6 % saccharose.

Variegated parts: no monose nor maltose, 0,7 % saccharose.

10. *Chlorophytum Sternbergianum* St. albo marginata.

Green parts: 1 % dir. reduc. sugar ¹⁾, saccharose 2,1 %.

Variegated parts: no monose, nor maltose, 2 % saccharose.

11. *Ophiopogon Jaburan* Lodd. albo marginata.

Green parts 0,2 % dir. reduc. sugar, saccharose 0,7 %.

Variegated parts: no monose, nor maltose, saccharose 1,8 %.

12. *Cyperus alternifolius* L. fol. var.

Green parts: 0,3 % dir. reduc. sugar (monose-reaction +) saccharose 2,4 %.

Variegated parts: no monose, nor maltose, saccharose 1,7 %.

¹⁾ Here BARFOED's reagent produced no positive reaction.

Discussion of the results.

From the facts above-stated it appears that all the subjects contain monoses as well as saccharose in the green parts, but also that in 10 of the 12 species there is a difference between the green and the variegated parts concerning the sugars they contain. The two species, *Cornus* and *Aesculus*, that did not reveal this difference contained monose and saccharose also in the variegated parts, although only a small amount of the latter was present in *Aesculus*. So we cannot draw any conclusions from these two subjects, but the case is different with the large majority (10 of the 12 species) exhibiting the strongly marked difference that in the variegated parts the monoses are lacking and saccharose is present.

This presence of monoses in the assimilating leaf-parts and the absence in the non-assimilating full-grown variegated leaves, in my opinion strongly favours the view that in the named subjects starch arises from monoses, nay, that the latter generally are the first sugars to be synthesised in the process of carbon assimilation. This is borne out by the fact that among the 10 species there are 3 viz. *Aspidistra*, *Chlorophytum* and *Ophiopogon*, that do not contain any starch as reserve-material. The latter substance is only present in the stomata of both the variegated and the green parts of the leaf.

Although the preceding exposition may be very favourable to this view, it can hardly be called a proof. Conclusive evidence, however, is adduced by the results obtained with *Pelargonium zonale*. We succeeded in depleting the full-grown leaves of the variegated *Pelargonium* of their sugar and starch by placing the plants in the dark for two or three times 24 hours. Apparently the plants were then quite normal, the leaves had not turned yellow, nor had they fallen off.¹⁾

Now when these plants were exposed to sunshine, monoses were the first sugars to be synthesized, and later on saccharose and starch, as appears from the above analyses. The monoses also increase sooner than the saccharose, which entirely corresponds with CAMPBELL's results. This researcher, however, did not work with sugar-free leaves, so that he could not observe the first appearance of the monoses, which is most conclusive.

¹⁾ With green varieties of *Pelargonium* we were not successful in this respect, neither with *Ilex Aquifolium* and *Saccharum officinarum* L. (hothouse). When branches of the holly or the sprouts of the sugarcane were enveloped in black hoods they still contained monoses and saccharose after a fortnight. Then they turned yellow (sugar-cane) or fell off (holly), so that the experiment was not continued.

We now have to look at the question which of the monoses is the primary product: is it glucose, or fructose, or do they come forth coincidentally? Formerly it was believed that the amount of either sugar present in vegetable extracts could be calculated by combination of the result of the polarimetric determinations with that of the reduction of FEHLING's solution, but critics have disqualified this method almost entirely ¹⁾.

Nor can the microchemical method of GRAFE ²⁾ for a differentiation of sugars be relied upon, as is shown by RUHLAND ³⁾.

Macrochemically different reactions can in the extract be exerted on fructose, for instance that of SELIWANOFF (heating of the solution with resorcin and hydrochloric acid). But saccharose also gives these reactions.

BROWN and MORRIS (l. c.), afterwards also PARKIN, came to the conclusion that fructose forms the main part of the monoses, and as they considered cane-sugar as the primary product, they believed to be justified in saying that less of the fructose that originated through inversion together with glucose is used up in metabolism, so that more of it remained.

This reasoning is not necessary from our point of view: that the formation of monoses is the primary process. That in one plant this configuration of monoses should be produced in excess, and in the other plant the other configuration, is not at all unlikely in consideration of the asymmetric structure of the enzyme-molecule.

Conversion of one configuration into the other is also conceivable. In the way used in the laboratory, viz. faintly alkaline environment, mannose is formed just as well as fructose and glucose. Taking into consideration that in the plant this mannose originates only if the mannans sometimes present are hydrolyzed, the way of conversion in the plant is probably not the same as in the laboratory.

Polarimetric determination by Mr. KUIPERS in the Chemical Laboratory of Groningen with extracts from the above-named plants, yielded at all times laevorotation with *Acer* and *Pelargonium*, dextrorotation with *Aesculus*, *Hedera*, *Aspidistra*, *Humulus* *Ilex* and *Chlorophytum*. We see then, that with *Acer* and *Pelargonium* laevorotation of fructose prevails and the dextrorotation of glucose and that saccharose; as has been said before determination of the quantity of monoses was unsuccessful.

¹⁾ DAVIS and DAISH, Journ. of agricultural Science 1913.

²⁾ GRAFE, Sitzber. d. Kais. Akad. d. Wiss. Wien 1905.

³⁾ RUHLAND, Jahrb. f. wiss. Botanik 1911. For the critique on the method see OFFNER, Zeitschr. physiol. Chem. 1905.

The extract from leaves of *Pelargonium*, which after being made sugarfree have assimilated during one hour, is also laevo-rotatory; the quantity of fructose calculated from the rotation, did, however, not agree with the amount calculated from the reduction, so that this question must be left for further investigation.

Finally we have to say something about the function of the saccharose.

In all the subjects examined saccharose was invariably met with in various quantities, as well in the variegated as in the green parts. I am of the opinion that it is to be considered as a condensation product of the monoses, which performs in the leaves the function of matter of transport just as according to BROWN and MORRIS¹⁾ this is probably the case in the germinating barley. Obviously this holds good for the full-grown variegated parts, as no other carbohydrate could be recognized in the leaf-stalks and in the veins. The very young parts should be inspected more narrowly, seeing that of the two subjects of which a sufficient quantity of purely white shoots were at my disposition, the one, *Acer Negundo*, contained also monoses and the other, *Humulus lupulus*, did not. Where does this monose in the young variegated parts of the maple take its origin? Has it been transported thither, or has it originated in situ from the transported saccharose?

We therefore, tried to ascertain whether invertase was present in the variegated parts. After BROWN and MORRIS (l. c.) the leaves were rapidly dried at 45° C., finely pounded in a mortar and the powder mixed with a saccharose solution. The addition of thymol was an adequate antiseptic, as the detection and estimation of the directly reducing sugar took place already after 12 hours, and the mixture was allowed to stand at 15° C. Then it was heated up to 80° C., and after the ordinary treatment with basic lead-acetate and disodium phosphate, the extract was examined²⁾ for directly reducing sugars.

Invertase appeared to be present in the variegated parts of *Acer Negundo*, *Humulus Lupulus*, *Euonymus Japonica*, *Ilex Aquifolium*, *Pelargonium zonale*, *Chlorophytum Sternbergianum*, *Aspidistra elatior*, i. e. all the plants of which an adequate amount of material was at our disposition.

1 Grm. of leaf-powder (variegated leaves) from *Acer Negundo* converts \pm 100 mgr. saccharose into invert-sugar within 12 hours

¹⁾ BROWN and MORRIS, Chem. Soc. 1890.

²⁾ The tissue did not contain dir. reducing sugar in the full-grown parts, so that all the monoses that might be present had come forth through inversion of the saccharose.

at 15° C. The powder of green leaves had about a similar inverting action.

Of the hop, of which the available material was most abundant, the enzyme was also obtained from the variegated parts by pounding the fresh leaves, by colation of the finely pounded mass, and subsequently treating the extract with excess of alcohol and dissolving the precipitate in water.

It is evident, therefore, that invertase is present in all variegated parts and the monoses in the very young leaves of *Acer Negundo* may have originated through inversion. When considering that the variegated leaves derive all their carbohydrates from the green ones, and that neither in the leaf-veins, nor in the leaf-stalks (except the lowermost part) of the full-grown leaves monoses are demonstrable, such a transport as monose will in these subjects be deemed highly improbable.

Now when saccharose is assumed to function as matter of transport, it is remarkable that both saccharose and invertase occur in the leaf-tissue and yet no monoses are distinguishable in the full-grown parts.

By thoroughly pounding these parts monoses are formed by autolysis e.g. in *Humulus lupulus* and in *Chlorophytum*, so that they are demonstrable in a few hours.

RUHLAND (l. c.) has broached the subject of localisation of sugar and enzyme in the Mangold (*Beta vulgaris*), and arrives at the conclusion that both will probably occur in the same cells, but the localisation in the cell is different. The saccharose is probably located in the vacuole, and the enzyme in the protoplasm.

An experimental inquiry in this direction goes beyond the capacity of our present equipment. True, SENFT's¹⁾ method indicates the localisation in the tissues, but because heating is required with saccharose, diffusion takes place, and hereby accurate localisation of the sugar is rendered impossible. Moreover we are entirely destitute of delicate reagents on the invertase.

Besides this question of localisation, the transport of saccharose from cell to cell involves new difficulties, since in passing through the protoplasm inversion can be expected. It might obviously be surmised that inactivation of the invertase comes into play here, since according to SÖRENSEN²⁾ it occurs already with a low concentration of the O. H.-ions. However, with a P_H -value of 8—10 (virage

¹⁾ SENFT, Sitzber. d. Kais. Akad. d. Wiss. in Wien 1904.

²⁾ SÖRENSEN, Biochem. Zeitschr. 1909.

phenolphthalein) the action of the invertase may be inhibited¹⁾ but is by no means arrested, while according to ATKINS²⁾ the P_H of the protoplasm is never larger than 8; of such an inactivation there is, therefore, no question.

Such monoses as might be formed, might also be used up directly in the dissimilation-processes; in the rapidly developing variegated growing-points and the young leaves of the hop monose is not demonstrable, as is indeed possible with those of *Acer Negundo*.

CONCLUSIONS.

1st. In the great majority (10 of 12) of the subjects examined there is a difference between the variegated and the green parts as regards the soluble sugars. The former contain only saccharose, the latter monoses and saccharose. This renders it probable that monoses are the primary carbohydrates in the assimilation process.

2nd. In the variegated leaves of *Pelargonium zonale*, freed of their sugar by placing them in darkness, monoses appear first with beginning assimilation, then follow saccharose and starch, which corroborates the conclusion sub 1.

3rd. Which of the monoses is primary has not yet been made out. In *Pelargonium zonale* fructose seems to preponderate among the formed monoses.

4th. The variegated, saccharose-containing parts of the leaves, contain also invertase. No adequate explanation can yet be given why in the presence of these two no inversion is noticeable in the living tissues. It is probable that difference in localisation of the two substances in the cell comes into play here.

1) The invertase from the leaf-powder of *Acer Negundo* as well as that of MERCK were active with a P_H value > 8 (MCLLVAIN'S Standard solution).

2) ATKINS, Notes Bot. School Trinity Coll. Dublin 1922.

Chemistry. — „*In-, mono- and plurivariant equilibria.*” XXV.

By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of January 26, 1924).

Components and composants.

In the previous communication we have seen that composition, thermodynamical potential, etc. of a phase may be represented also with the aid of composants. We now shall discuss in this way some properties, which have been deduced formerly with the aid of components.

We take a system of n components, wherein an equilibrium $E = F + L$ occurs; F represents a solid phase with constant composition, L a liquid.

We assume that an equilibrium $E_0 = F + L_0$ exists at a temperature T_0 . We now bring this equilibrium from the temperature T_0 towards $T_0 + dT$, while we imagine the pressure to be constant; the new equilibrium which we shall call $E = F + L$, arises from E_0 by the fact that a little of the solid substance F dissolves or crystallises.

As the equilibrium consists of n components, we may represent it also with the aid of n composants; for this we take the solid substance F , the liquid L_0 and still also $n-2$ arbitrary substances $N P \dots$. Therefore, we may represent an arbitrary liquid L by

$$L = m F + n L_0 + p P \dots + (1 - m - p \dots) L_0 \quad (1)$$

in which case L_0 has been chosen as fundamental composant.

For an equilibrium $E = F + L$, wherein L is defined by (1), at an arbitrary temperature T the following equation is valid:

$$\zeta - (m-1) \frac{\partial \zeta}{\partial m} - n \frac{\partial \zeta}{\partial n} - \dots = \zeta_1 \quad (2)$$

wherein ζ and ζ_1 represent the thermodynamical potentials of L and F .

For a temperature $T + dT$ then is valid the equation:

$$(1-m) d \frac{\partial \zeta}{\partial m} - n d \frac{\partial \zeta}{\partial n} - \dots = (\eta - \eta_1) dT \quad (3)$$

wherein the sign d indicates that there must be differentiated for all variables, also for T .

We take a liquid L , which differs in composition uninfinitely little from L_0 ; it appears from (1) that m , n etc. then are uninfinitely small; instead of (3) we then may write:

$$d \frac{\partial \zeta}{\partial m} = \frac{\partial^2 \zeta}{\partial m^2} dm + \frac{\partial^2 \zeta}{\partial m \partial n} dn \dots = \left(\eta - \eta_1 + \frac{\partial \eta}{\partial m} \right) dT \dots \quad (4)$$

As, however, we have under consideration an equilibrium $E = F + L$, wherein L arises from L_0 by solution or crystallisation of a little of the solid substance F , then dn , dp etc. are zero. Consequently we get:

$$r dm = \left(\eta - \eta_1 + \frac{\partial \eta}{\partial m} \right) dT \dots \quad (5)$$

wherein the meaning of r follows from (4). The coefficient of dT is increase of entropy when the solid substance F dissolves in the liquid L_0 . Consequently the sign of this coefficient is the same as that of the heat of solution of the solid substance F in the liquid L_0 . As $r > 0$, we find for a system with an arbitrary number of components:

at increase of temperature the solubility of a solid substance increases, when the heat of solution is positive, the solubility decreases when the heat of solution is negative¹⁾.

When we imagine the equilibria to be represented graphically, then we may say also:

on increase of temperature the region of liquid shifts towards the solid substance, when the heat of solution is positive, but it shifts away from the solid substance, when the heat of solution is negative.

A corresponding rule is true, of course, for the influence of a change in pressure.

When an equilibrium $E_0 = F + L_0$ exists at T_0 , then at the same temperature yet also other equilibria $E = F + L$ exist; they are defined by (3) when we omit herein all terms with ΔT . When we take under consideration liquids L which differ infinitely little from L_0 , then (3) passes into (4) wherein the term with ΔT is disappearing then. When we limit ourselves to a ternary system, then (4) passes into:

$$r dm + s dn = 0 \dots \quad (6)$$

¹⁾ Compare a.o. F. A. H. SCHREINEMAKERS; Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM III¹. 270.

Hence follows at once the known property¹⁾:

the tangent in an arbitrary point L_0 to the saturation-curve of a solid substance F and the conjugation-line $L_0 F$ are conjugated diameters of the indicatrix in the point L_0 .

As the composant N is still arbitrary, we shall choose it now in such a way that s becomes $= 0$. Now (6) passes into $r dm = 0$. When we introduce in (3) also the term with dn^2 , then we obtain instead of (6):

$$2r dm = \left(t - \frac{\partial t}{\partial m} \right) dn^2 \quad (7)$$

Consequently the saturation-curve is curved parabolically in each point; when, however, accidentally, the coefficient of dn^2 is zero, then the point under consideration is a point of inflexion.

For an equilibrium $E = F + L$, wherein

$$L = m M + n N + (1 - m - n) F$$

is true at a temperature T

$$\zeta - m \frac{\partial \zeta}{\partial m} - n \frac{\partial \zeta}{\partial n} \dots = \zeta_1 \quad (8)$$

At the melting-point T_0 of the solid substance F , L gets the composition F , so that $m, n \dots$ are zero. We now take at the temperature $T_0 + \Delta T$ an equilibrium $E = F + L$, wherein L differs infinitely little from F . As $m, n \dots, \Delta T$ are infinitely small, (8) passes into:

$$- \left(m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \dots \right)^{(2)} = 2 (\eta - \eta_1) \Delta T \quad (9)$$

wherein the terms, which are infinitely small with respect to those which are written-down, are omitted. As the first part of (9) is negative and $\eta - \eta_1$ is positive, consequently we have to take ΔT negative. The equilibrium $F + L$ exists, therefore, only below the melting-point T_0 of the substance F . For a ternary system (9) passes into:

$$- (rm^2 + 2smn + tn^2) = 2 (\eta - \eta_1) \Delta T \quad (10)$$

The saturation-curve of F is, therefore, a small ellipsis, which has as centre the point F .

We take a ternary equilibrium $E = F + F_1 + L$, wherein F and F_1 are solid substances with constant composition, and L a liquid with variable composition. We assume that an equilibrium

¹⁾ I. c. III 72, 264.

$E_0 = F + F_1 + L_0$ exists at a temperature T_0 . We represent the composition of L by:

$$L = m F + n F_1 + (1 - m - n) L_0.$$

For the equilibrium $E = F + L$ we find:

$$\zeta + (1 - m) \frac{\partial \zeta}{\partial m} - n \frac{\partial \zeta}{\partial n} = Z \quad . \quad . \quad . \quad (11)$$

for the equilibrium $E = F_1 + L$

$$\zeta - m \frac{\partial \zeta}{\partial m} + (1 - n) \frac{\partial \zeta}{\partial n} = Z_1 \quad . \quad . \quad . \quad (12)$$

both equations are valid for $E = F + F_1 + L$.

Equation (11) represents the saturation-curve of the substance F ; when we take a liquid L , which differs only extremely little from L_0 , then m and n approach to zero. Then we may write for (11):

$$m \frac{\partial^2 \zeta}{\partial m^2} + n \frac{\partial^2 \zeta}{\partial m \partial n} = 0 \quad . \quad . \quad . \quad (13)$$

From (12) it follows:

$$m \frac{\partial^2 \zeta}{\partial m \partial n} + n \frac{\partial^2 \zeta}{\partial n^2} = 0 \quad . \quad . \quad . \quad (14)$$

When we give the index 1 to m and n in (14) then we may write for (13) and (14):

$$\frac{m}{n} = -\frac{r}{s} \quad \frac{n_1}{m_1} = -\frac{s}{t} \quad . \quad . \quad . \quad (15)$$

wherein the meaning of r s and t is clear.

As r and t are both positive, consequently $n:m$ and $n_1:m_1$ have the same sign. When both ratio's are positive, then the two saturation-curves are situated within the conjugation-angle $F L_0 F_1$; when both ratio's are negative, then the two saturation-curves are situated without the conjugation-angle $F L_0 F_1$. Therefore, here we find the property¹⁾ which is deduced already formerly in another way: in the point of intersection L_0 of the saturation-curves of F and F_1 those curves are situated either both within the conjugation-angle or both without that angle.

In the deduction above there is supposed that r and t are positive; therefore the property is certainly true when the liquid taken for itself, is stable. When, however, it is instable (consequently when it is situated within the spinodal-curve $rt - s^2 = 0$) then r or t may

¹⁾ l. c. III^a 72, 264.

be negative also; the one curve then may be situated within and the other out of the conjugation-angle¹⁾.

For the equilibrium $E = F + F_1 + L$ at the temperature $T_0 + dT$ we have to introduce in (13) and (14) still also terms with dT . We find:

$$\left. \begin{aligned} mr + ns &= \left(\eta + \frac{\partial \eta}{\partial m} - H \right) dT = \frac{W}{T_0} dT \\ ms + nt &= \left(\eta + \frac{\partial \eta}{\partial n} - H_1 \right) dT = \frac{W_1}{T_0} dT \end{aligned} \right\} \dots \dots (16)$$

wherein W and W_1 are the heats of solution of F and F_1 in the liquid L_0 . It follows from (16):

$$T_0 (rt - s^2) m = (tW - sW_1) dT \dots \dots (17)$$

$$T_0 (rt - s^2) n = (rW_1 - sW) dT \dots \dots (18)$$

The direction of the saturation-curve of $F + F_1$ in the vicinity of the point L_0 follows from those equations. When m and n are both positive or negative, then this curve is situated within the conjugation-angle FL_0F_1 ; then it is a curve of melting or solution; when m and n have opposite signs, then the curve is situated out of the conjugation-angle FL_0F_1 and it is a curve of conversion.

We now are able to deduce from (17) in connection with (15) several properties. When f.i. we assume that the two heats of solution W and W_1 are positive; when $s < 0$ then the coefficients of dT in (17) and (18) are positive and m and n consequently also; when $s > 0$ then both coefficients and consequently also m and n may have as well the same sign as different sign.

Hence it follows, assuming that the heats of solution of F and F_1 are both positive: when the two saturation-curves of F and F_1 are situated within the conjugation-angle FL_0F_1 then the saturation-curve of $F + F_1$ is situated also within that angle; when the two saturation-curves of F and F_1 are situated out of the conjugation-angle, then the saturation-curve of $F + F_1$ may be situated as well within as out of that angle.

We assume that the equilibrium $E = F + F_1 + L$ passes at a temperature T_0 into $E_0 = F + F_1 + L_0$ wherein a phases-reaction may occur between the three phases. Now we consider the equilibrium $E = F + F_1 + L$ at a temperature $T_0 + \Delta T$. We represent the phases-reaction by

$$F = \alpha F_1 + (1 - \alpha) L_0 \dots \dots (19)$$

¹⁾ l. c. III² 340.

and we take, besides F_1 and L_0 , also an arbitrary composant M . We then may put:

$$L = m M + n F_1 + (1 - m - n) L_0$$

For the equilibrium $F + L$ we find:

$$\zeta - m \frac{\partial \zeta}{\partial m} - (n - a) \frac{\partial \zeta}{\partial n} = Z$$

for the equilibrium $F_1 + L$ follows ($a = 1$):

$$\zeta - m \frac{\partial \zeta}{\partial m} - (n - 1) \frac{\partial \zeta}{\partial n} = Z_1.$$

For a temperature $T = T_0 + \Delta T$ m and n approach to zero; when we take also terms of the second order of m and n , the equations above pass into:

$$a \left(d \frac{\partial \zeta}{\partial n} + \frac{1}{2} d^2 \frac{\partial \zeta}{\partial n} \right) - \frac{1}{2} A = (\eta - H) \Delta T$$

$$\left(d \frac{\partial \zeta}{\partial n} + \frac{1}{2} d^2 \frac{\partial \zeta}{\partial n} \right) - \frac{1}{2} A = (\eta - H_1) \Delta T$$

wherein: $A = r dm^2 + 2 s dm dn + t dn^2$.

Hence it follows:

$$-\frac{1}{2} A = \frac{(1-a)\eta + a H_1 - H}{1-a} \cdot \Delta T$$

Now the coefficient of ΔT is the increase of entropy when one quantity of liquid is formed at reaction (19). When we assume that at this reaction heat must be added, then this coefficient is positive. As A is positive also, it follows that we may give only negative values to ΔT . As, further, ΔT is of the order of m^2 we have also:

$$d \frac{\partial \zeta}{\partial n} = s dm + t dn = 0.$$

From all this it follows: when in the equilibrium $E = F + F_1 + L$ the liquid L gets such composition, that a phases-reaction is possible between the 3 phases, then the temperature is a maximum. The saturation-curves of F of F_1 and of $F + F_1$ touch one another in one point; this represents the liquid mentioned above.

We now take an equilibrium $E = F + F_1$ wherein F and F_1 have variable composition; f.i. mixed-crystal, liquid or vapour. We assume that an equilibrium $E_0 = (F)_0 + (F_1)_0$ exists at a temperature T_0 . When we take besides $(F)_0$ and $(F_1)_0$ also $n-2$ arbitrary composants, then we may put:

$$F = m (F_1)_0 + n N \dots + (1 - m - n \dots) (F)_0$$

$$F_1 = m_1 (F_1)_0 + n_1 N \dots + (1 - m_1 - n_1 \dots) (F)_0$$

For the equilibrium $E = F + F_1$ at a temperature T' then the following n equations are valid:

$$\zeta - m \frac{\partial \zeta}{\partial m} - n \frac{\partial \zeta}{\partial n} \dots = \zeta_1 - m_1 \frac{\partial \zeta_1}{\partial m_1} - n_1 \frac{\partial \zeta_1}{\partial n_1} \dots$$

$$\frac{\partial \zeta}{\partial m} = \frac{\partial \zeta_1}{\partial m_1} \quad \frac{\partial \zeta}{\partial n} = \frac{\partial \zeta_1}{\partial n_1} \text{ etc.}$$

We now take the equilibrium $E = F + F_1$ at a temperature $T_0 + \Delta T$ and take care that F and F_1 differ infinitely little from $(F)_0$ and $(F_1)_0$. All variables then approach to zero, excepted m_1 which approaches to 1. The previous equations now pass into:

$$\eta \Delta T + \frac{1}{2} A = \eta_1 \Delta T + d \frac{\partial \zeta_1}{\partial m_1} \dots \dots \dots (20)$$

$$d \frac{\partial \zeta}{\partial m} = d \frac{\partial \zeta_1}{\partial m_1} \quad d \frac{\partial \zeta}{\partial n} = d \frac{\partial \zeta_1}{\partial n_1} \text{ etc.} \dots \dots \dots (21)$$

wherein

$$A = \left(\frac{\partial \zeta}{\partial m} \cdot dm + \dots \right)^{(2)}$$

With the aid of the first equation (21) we also may write for (20):

$$d \frac{\partial \zeta}{\partial m} = (\eta - \eta_1) \Delta T \dots \dots \dots (22)$$

Amongst all changes which the phase $(F)_0$ may endure, we now take only that which occurs by the fact that $(F)_0$ takes up or separates a little of $(F_1)_0$. All variations of phase F , excepted dm then are zero; (22) now passes into:

$$r dm = \left(\eta + \frac{\partial \eta}{\partial m} - \eta_1 \right) \Delta T \dots \dots \dots (23)$$

The variations of the phase F_1 are defined now by the $n-1$ equations (21). In a similar way as from (5) for the equilibrium $E = F + L$, we now find from (23) for the equilibrium $E = F + F_1$:

at increase of T the region of the phase F moves towards the region of F_1 when the heat of solution of F_1 in F is positive; but it moves away from the region of F_1 when this heat of solution is negative.

We now consider the equilibrium $E = F + F_1$ at the temperature T_0 ; then we must put in (21) and (22) $\Delta T = 0$. When we neglect data of higher order, then they pass into:

$$d \frac{\partial \xi}{\partial m} = 0 \quad d \frac{\partial \xi_1}{\partial m_1} = 0 \quad d \frac{\partial \xi}{\partial n} = d \frac{\partial \xi_1}{\partial n_1} \text{ etc.} \quad (24)$$

Consequently we have n relations between the $2n-2$ variations. For a ternary system ($n=3$) it follows:

$$\left. \begin{aligned} r dm + s dn &= 0 & r_1 dm_1 + s_1 dn_1 &= 0 \\ s dm + t dn &= s_1 dm_1 + t_1 dn_1 \end{aligned} \right\} \quad (25)$$

Consequently each of the phases of the equilibrium is represented by a curve; when f.i. F and F_1 are liquids, then this is the binodal-curve. From (25) it also appears again that the conjugation-line FF_1 and the tangent in F (and F_1) to the curve of equilibrium, are conjugated diameters of the indicatrix in F (and F_1).

From (25) it follows:

$$\frac{dn}{dn_1} = \frac{r(r_1 t_1 - s_1^2)}{r_1(rt - s^2)} \quad (26)$$

When F and F_1 are stable phases, then dn and dn_1 have, therefore, the same sign. This means: when we pass from an equilibrium $E_0 = (F)_0 + (F_1)_0$ into an equilibrium $E = F + F_1$ then the new phases F and F_1 are situated on the same side of the conjugation-line $(F)_0(F_1)_0$.

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(To be continued).

Chemistry. — “*The Metastability of the Elements and Chemical Compounds in consequence of Enantiotropy or Monotropy.*”
IV. By Prof. ERNST COHEN and J. KOOY.

(Communicated at the meeting of December 29, 1923).

1. We have shown in several papers with the above title¹⁾ that many, if not all, substances are mixtures of several allotropic modifications, as a consequence of the reluctance they display in undergoing transformation.

As a result of this, the physical properties which have hitherto been assigned to these substances are those of a mixture of unknown composition, so that they are actually without meaning.

It follows accordingly that the determination of the physical constants of the *pure* substances must be looked upon as an important task.

The present research is concerned with showing — together with quantitative proof — to what completely erroneous results the ignoring of this fact in former contributions in this field can lead.

2. FRANKENHEIM²⁾ had already discovered in the year 1854 that ammonium nitrate is polymorphic. While this author only describes two modifications of the salt, O. LEHMANN³⁾ was later able to show that five stable modifications are capable of existence at atmospheric pressure. A few years ago BRIDGMAN⁴⁾ found a sixth, which is only stable under high pressure.

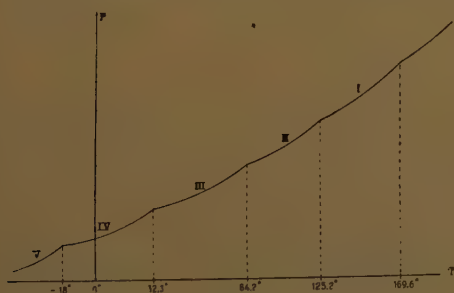


Fig. 1.

Fig. 1 shows in a qualitative manner the p - t -diagram of the

¹⁾ Zeitschr. f. physik. Chemie 94, 450, 465, 471 (1920).

²⁾ Pogg. Ann. 93, 17 (1854).

³⁾ Dissertation Strassburg 1876; Zeitschr. f. Kristallogr. 1, 97 (1877). WALLERANT, Bull. Soc. franc. de minéralogie 1905, p. 311. C. R. 142, 217 (1906). BEHN, Proc. Roy. Soc. London (A) 80, 444 (1908).

⁴⁾ Proc. Americ. Acad. of Arts and Sciences 51, 581 (1916).

modifications which can appear in a stable form at atmospheric pressure. Whilst the melting-point lies at 169.6, the following transformations are possible:



The different modifications crystallize in the following forms: I, cubic; II, hexagonal-rhomboëdric; III, β -rhombic; IV, α -rhombic; V, tetragonal¹⁾.

For general orientation it should be noted that the change $\text{I} \rightarrow \text{II}$ is accompanied by a contraction; $\text{II} \rightarrow \text{III}$ by an expansion; $\text{III} \rightarrow \text{IV}$ by a contraction; and $\text{IV} \rightarrow \text{V}$ by an expansion.

3. The fact that the majority of the workers in this field have found values for the transition temperature of $\text{III} \rightleftharpoons \text{IV}$ ²⁾ which differ very widely from another according as they worked with a rising or falling temperature (the extreme values fall between 31 and 36 degrees) already indicates the strong reluctance exhibited in these changes.

Moreover BEHN found that II could be supercooled from 83° to 45° without the corresponding change taking place. Reference must also be made here to BEHN's communication that V itself undergoes no change in contact with IV at 18°.

BRIDGMAN makes the general deduction from his experiments, that "*ammonium nitrate is a substance for which it is particularly difficult to force the reaction from one phase to another to run to completion.*" He has also observed this with other substances, therefore in complete agreement with our earlier work.

4. Now there were carried out by BRIDGMAN a number of exceedingly careful investigations into the thermodynamic conditions of numerous substances, amongst which is included ammonium nitrate³⁾. In these, where he deals with the influence of pressure on the polymorphic transformations of univalent nitrates, he determined experimentally the value, amongst others for ammonium nitrate, of

$$\frac{dT}{dp} \text{ and } (v_{\text{III}} - v_{\text{IV}})$$

¹⁾ With reference to the important question as to whether II and IV are identical, reference should be made to the papers of BEHN and WALLERANT: Note 3, p. 65. Also BRIDGMAN: Note 4, p. 65.

²⁾ A collection of data will be found in EARLY and LOWRY, Journ. Chem. Soc. London 115, 1887 (1919).

³⁾ Proc. Americ. Acad. of Arts and Sciences 51, 581 (1916).

which appear in the equation of CLAPEYRON-CLAUSIUS:

$$\frac{dT}{dp} = \frac{T(v_{III}-v_{IV})}{W}$$

and calculates from this the value of W .

Here as usual p is the pressure, T the absolute temperature of transition for the particular modifications, v_{III} and v_{IV} their specific volumes at that temperature, W the heat of transformation.

Table I gives the data for the transformation $III \rightleftharpoons IV$.

TABLE I.

| Press. in kg/cm ² . | Temp. | $v_{III}-v_{IV}$ ccs. per gm. | $\frac{dT}{dp}$. |
|-----------------------------------|-------|----------------------------------|-------------------|
| 1 | 32°.0 | 0.02026 | 0.0311 |
| 200 | 38°.5 | 0.02051 | 0.0336 |
| 400 | 45°.4 | 0.02077 | 0.0360 |
| 600 | 52°.9 | 0.02102 | 0.0385 |
| 800 | 60°.8 | 0.02128 | 0.0410 |

On the ground of the above communication it appears to us very probable that the values given here for $v_{III}-v_{IV}$ must be erroneous: actually, on account of the reluctance referred to, too small. If this is actually the case, the proof is given afresh that on account of the metastability of substances value can only be assigned to physical constants when these are determined for *pure* modifications of these substances.

5. We have set ourselves the task of determining by different methods the value of $v_{III}-v_{IV}$ for ammonium nitrate at the transition temperature and under atmospheric pressure, in order to compare these with those determined by BRIDGMAN.

The latter found at 32°.0 C. the value $(0.02026 \frac{cc.}{gm.}$ Table I), by measuring the displacement of the piston in a pressure apparatus in which the transformation $IV \rightleftharpoons III$ took place.

Older Determinations of $(v_{III}-v_{IV})$.

6. We find two values given in the literature, of which that of

BRIDGMAN is noted above. BELLATI and ROMANESE¹⁾ embody their measurements on the modification IV in the equation:

$$(v_{IV})_{t^0} = v_0 (1 + 0.000339t + 0.000000.346t^2) \quad . \quad . \quad (1)$$

which holds between 0° and 35°.

For the modification III they find:

$$(v_{III})_{t^0} = v_0 (1.04957 - 0.00038756t + 0.000008976t^2 - \\ 0.000.0000432t^3). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which is valid for the temperature interval 40°—85°. In these equations v_0 is the specific volume of IV at 0° C.

The authors found the transition point with rising temperature at 35°, with falling temperature at 31°. If we assume with them, quite arbitrarily, that 35° is the true transition point, we obtain from (1): $(v_{IV})_{35^0} = 1.01228 v_0$ from (2): $(v_{III})_{35^0} = 1.04514 v_0$, thence for the volume change, $(v_{III} - v_{IV})_{35^0} = 0.03286 v_0$.

Now BELLATI and ROMANESE found the value 1.674 for the density of IV at 0° C., and believe they find a confirmation of the accuracy of this figure in the fact that the latter is exactly the mean of the values that JOULE and PLAYFAIR (1.635, in three determinations), and SCHRÖDER (1.737, in two determinations), have found respectively.

From these figures we obtain according to BELLATI and ROMANESE the value $0.01963 \frac{cc.}{gm.}$ for $(v_{III} - v_{IV})_{35^0}$.

The calculation shows without further discussion that little significance can be assigned to this result.

A second determination of the volume-change in question we owe to BEHN²⁾. A complete paper is not available. His communication indicates that he has found by a dilatometric method the temperature 32° for the transition point, and that the corresponding volume-change amounts to 3.8% of the volume at 20°; while he found for the density of IV the value 1.725 at 20°. The value of $(v_{III} - v_{IV})$ at 32° calculated from these data becomes $0.022 \frac{cc.}{gm.}$ which differs by no less than 12% from that of BELLATI and ROMANESE.

¹⁾ Atti del R. Istituto Veneto 4 (VI) 1395 (1886). Also Il nuovo Cimento (3) 21, 1 (1887).

²⁾ See note 3 page 65.

*Determination of ($v_{III}-v_{IV}$).**A. Determination of the Transition Temperature.*

7. Since we wish to find ($v_{III}-v_{IV}$) at the transition temperature, and the latter has been assigned very different values by different authors, as indicated above, we have first concerned ourselves with the determination of this as accurately as possible. When our experiments were already completed we found that EARLY and LOWRY¹⁾ had carried out actually a few years previously a comprehensive investigation in this direction. It will appear that our results agree very closely with those of the authors mentioned.

The ammonium nitrate used by us we prepared by repeated recrystallisation of a fairly pure preparation, and drying of the product over P_2O_5 (which was frequently renewed) in vacuo. Since the salt retains water very persistently we frequently ground it up so as to open up any vacuoles present. This was continued until there was no longer any appreciable loss in weight in three days. Impurities could not be detected in the end-product obtained, whilst 5 gm. of the salt left no residue on heating.

A preliminary dilatometric experiment (with a dilatometer of about 50 ccs. capacity) gave the results shown in Table II.

TABLE II.

| Temperature. | Displacement of the meniscus in the capillary, in 45 minutes. |
|--------------|--|
| 33°.0 | + 75 mm. |
| 32°.1 | — 25 " |
| 32°.5 | + 25 " |
| 32°.3 | 0 " |

EARLY and LOWRY determined the transition temperature, by a dilatometric method, to be 32°.1. Since the above experiment gave a result differing by about 0°.2, we repeated it with a larger mass of the salt. EARLY and LOWRY worked with a dilatometer of about 60 cc. capacity, which they filled three-quarters full of the salt. We used a similar one of about 100 cc. capacity, into which 65.6 gms of the salt was introduced, which had been dried for a month over

¹⁾ Journ. Chem. Soc. London 115, 1387 (1919).

sulphuric acid. Our capillary had a bore of 1 mm. (EARLY and LOWRY do not give the diameter of their capillary). We first changed 50 % of the modification IV into III, and studied the volume change in the thermostat at different temperatures. Table IIa gives the data.

TABLE IIa.

| Temperature. | Time in hours. | Displacement of the meniscus in mm. | Displacement per hour. |
|--------------|----------------|-------------------------------------|------------------------|
| 32°.16 | 24 | — 126.3 | — 5.2 |
| 32°.18 | 17½ | — 27 | — 1.5 |
| 32°.24 | 20⅓ | — 5.7 | — 0.28 |
| 32°.30 | 25 | — 1 | — 0.04 |
| 32°.40 | 12 | + 1 | + 0.08 |
| 32°.50 | 23 | + 29 | + 1.3 |

Thus we find the transition temperature at 32°.3, as in the first, orientating experiment.

Our thermometer (divided in 1/10ths degrees), which was standardised by the Phys. Techn. Reichsanstalt at Charlottenburg-Berlin, was also checked by ourselves, when we established that it had not altered its zero-point.

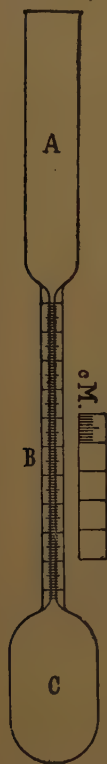
B. First Method for the determination of (v_{III} — v_{IV}).

8. This consists in ascertaining independently the value of v_{III} and v_{IV} respectively at the transition temperature. Since we had determined v_{III} at 32°.50 and v_{IV} at 32.00° for other purposes by the elegant method which was described by ANDREAE¹⁾ for the determination of density of solid substances (salts), we give first our results obtained in this connection. By means of a correction the values of the specific volumes of the two modifications found in this way can be recalculated for the transition temperature.

This method has two disadvantages: firstly the introduction of the correction mentioned, and secondly the fact that very small errors in the determination of the quantities which enter in this calculation, affect the result to an extent that cannot be ignored. The second method, to be described later, is therefore to be preferred.

¹⁾ Zeitschr. f. physik. Chemie 82, 109 (1913).

9. Since we had to depart from the method described by ANDREAE on account of the peculiar properties of ammonium nitrate, which is volatile both in the dry state and with water-vapour at 100° , we give a somewhat detailed account here of the experimental technics.



The pyrometer used (Fig. 2) held about 25 cc. The tube *B* is about 3 mm. wide and is divided into millimeters. It ends in a funnel *A*. After each experiment the volume of the bulb was determined together with that of the tube *B* by weighing out with water up to the mark at which the meniscus made by the contents had stood at the temperature of the experiment. After the dried apparatus was weighed, a solution of the salt saturated at about 100° was introduced into it and it was placed in a thermostat. We determined v_{IV} at $32^{\circ}.00$, v_{III} at $32^{\circ}.50$.

After the excess of salt had crystallised out, the bulb *C* was warmed until the salt had again gone completely into solution. Any air present then escaped. The apparatus was placed once more in the thermostat, turned continuously backwards and forwards on its vertical axis to hasten the saturation, and kept at $32^{\circ}.00$ until the meniscus in *B* showed no change.

One was assured then that the solid salt had actually changed into the form IV. Further assurance was given on this point by bringing the salt, after the first experiment, partly or completely into solution by warming the apparatus, and observing if the meniscus occupied again the same position at $32^{\circ}.00$. If this was the case, the position was noted.

Then the pyrometer was weighed with its contents.

We carried out all weighings on a BUNGE balance (to 0.1 mgm.); and corrected to vacuum. The weights used were standardised by the method described by KOHLRAUSCH¹⁾.

The apparatus was emptied, after all the salt had been brought into solution by heating, and the solution was transferred quantitatively into a measuring-flask²⁾ of 500 cc. capacity. Then followed the exact determination of the quantity of ammonium nitrate that was present in the pyrometer; 50 cc. of the solution was used each time for this purpose.

¹⁾ Lehrbuch der prakt. Physik. 11. Aufl. Leipzig 1910, p. 62.

²⁾ The measuring-flasks, pipettes and burettes used were carefully standardised.

10. The method of estimation used, that of L. W. WINKLER¹⁾ is so accurate that the fact that only $\frac{1}{10}$ of the solution was taken is of no moment. 50 cc. were heated with excess of ammonia-free caustic soda solution, the ammonia evolved led into a cold saturated solution of boric acid (with solid particles), and this was titrated back with hydrochloric acid, using methyl orange as an indicator. The colour-change is uncommonly sharp.

The hydrochloric acid used was standardised as follows. An exactly weighed quantity of the purest ammonium chloride is heated with excess of caustic soda solution. The ammonia evolved is led into boric acid as described above and titrated with the hydrochloric acid whose strength is to be determined.

That the method described is very exact may be shown e.g. by the following experiment: 2.4443 gm. NH_4NO_3 weighed out; 61.73 cc. of 0.4948 N HCl used: therefore NH_4NO_3 found 2.4449 gm.

It should be further noted that in the analysis of the solutions from the pycnometer fairly large quantities of hydrochloric acid (about 60 cc.) were always used: errors of reading are therefore negligible.

11. If m_1 is the weight of ammonium nitrate present in the pycnometer, which will therefore be estimated analytically after the experiment;

m_2 the weight of the salt together with the solvent;

v_s the specific volume of the salt which has to be determined, at the temperature of the experiment;

c the concentration of the solution saturated at this temperature, expressed in gm. salt per gm. solvent;

v_c the specific volume of the saturated solution at that temperature;

V the volume of the bulb C plus that of the tube B up to the mark at which the meniscus stands;

then: ²⁾

$$v_s = \frac{V - (1 + c)(m_2 - m_1)v_c}{m_1 - (m_2 - m_1)c} \quad \dots \quad (1)$$

In order to calculate v_s we have therefore to determine the specific volume v_c of the saturated solution as well as the solubility c at the temperature of the experiment.

¹⁾ Zeitschr. f. angewandte Chemie 26, 231 (1913); 27, 630 (1914).

²⁾ ERNST COHEN and A. L. TH. MOESVELD. Zeitschr. f. physik. Chemie 93, 385 (1919).

We have determined those quantities independently, since their values, where they are to be found in the literature, do not appear to us to be sufficiently well established ¹⁾.

Determination of v_c and c at 32°.00 and 32°.50 C.

12. To determine v_c we shook up an excess of the salt with unsaturated or supersaturated solutions respectively. The apparatus used was one that has been described previously ²⁾. Since the temperature coefficient of solubility of ammonium nitrate is very appreciable, the temperature was held constant within 0°.01. (The toluene regulator held 500 cc.). Supersaturated solutions reached equilibrium in about 50 minutes; unsaturated solutions after 48 hours.

We determined the density of the saturated solutions by means of a SPRENGEL-OSTWALD-EYKMAN pyknometer ³⁾. Crystallising-out of the salt was prevented by immersing the pyknometer wholly under the water in the thermostat used. After chem. cand., C. v. D. BUNT had carried out some determinations at 32°.00. which gave the following results:

$$d_4^{32°.00} = 1.3321^1; 1.3321^1; 1.3321^0; 1.3321^1,$$

we repeated the measurements with another preparation and found: 1.3322², 1.3321¹, 1.3322². As mean value we took 1.3322.

Accordingly

$$(v_c)_{32°.00} = 0.75064.$$

At 32°.50 C. the results were:

$$d_4^{32°.50} = 1.3329^1; 1.3328^1; 1.3329^0.$$

Mean 1.3329,

Then $(v_c)_{32°.50} = 0.75024.$

13. To determine the solubility of ammonium nitrate the saturated solutions were analysed according to the method of WINKLER already described. Table III gives the experimental results.

¹⁾ Solubility determinations for ammonium nitrate at the transition temperature are described by WOLF MÜLLER and KAUFMANN, *Zeitschr. f. physik. Chemie* **42**, 497 (1903); PAUL MONDAIN MONVAL, *C. R. Paris* **177**, 175 (1923).

²⁾ ERNST COHEN and H. R. BRUNS, *Zeitschr. f. physik. Chemie* **93**, 43 (1918)

³⁾ *Rec. des Trav. Chim. des Pays-Bas* **13**, 13 (1894).

TABLE III.
Determinations of Solubility of NH_4NO_3 .

| Temperature 32°.00 C. | | | | | | |
|------------------------|----------------------------------|-------------------|------------------------------|---|------------------------------|------------------|
| Time of shaking hours. | Weight of saturated solution gm. | cc. HCl 0.4948 N. | gm. NH_4NO_3 | gm. salt in 100 gm. saturated solution. | gm. salt in 1 gm. solvent c. | Mean value of c. |
| 54 | 5.2052 | 92.87 | 3.6782 | 70.67 | 2.4088 | 2.410 |
| 100 | 2.4383 | 43.52 | 1.7236 | 70.69 | 2.4116 | |
| Temperature 32°.50 C. | | | | | | |
| 3 | 3.3049 | 59.08 | 2.3400 | 70.89 | 2.4251 | 2.426 |
| 3½ | 3.0142 | 53.90 | 2.1348 | 70.82 | 2.4276 | |

In connection with this table it must be noted that the equilibrium at 32°.00 was reached from the side corresponding to unsaturated solutions. We are too near here to the transition temperature to be able to start with *supersaturated* solutions. On the other hand the equilibrium at 32°.50 was reached from the side of *supersaturated* solutions.

14. We will compare the figures obtained at 32°.00 with those that v. D. BONT determined for us with another preparation and in

TABLE IV.

| Concentration: gm. salt weighed out for 100 gm. solution. | Density found: 32°.00 d_{40}° | gm. salt per 100 gm. solution. Calculated. |
|--|--|---|
| 24.51 | 1.09703 | — |
| 38.97 | 1.16394 | 38.95 |
| 49.95 | 1.21851 | 49.95 |
| 54.91 | 1.24434 | — |
| 59.88 | 1.27104 | 59.89 |
| 66.73 | 1.30938 | — |

a different manner. He measured the density of a number of solutions of different concentrations (obtained by weighing out definite quantities). A curve was thus obtained which showed the concentration as a function of the density. If the density is now determined, by a pyknometric method, of the solution saturated at $32^{\circ}.00$, we can find the corresponding concentration from this curve. Table IV gives the results obtained by this method. (See p. 74).

From the values obtained in the first, fourth, and sixth experiments, we get:

$$c = -360.23 + 477.97 d - 116 d^2.$$

If from this equation we calculate the concentrations as made up by weighing-out the salt in the second, third and fifth experiments, we find the figures given in the third column. If we substitute in the equation the value which we found for the density of the saturated solution (1.3322), we obtain $c = 70.65$, in close agreement with that found by us in another manner ($c = 70.68$, Table III).

15. If we now put in equation (1), p. 72, the numerical values as collected in Table V, we find:

$$(v_{IV})_{32^{\circ}.00} = 0.58250.$$

$$(v_{III})_{32^{\circ}.50} = 0.60465.$$

To reduce these values for v_{IV} and v_{III} respectively to the transition temperature we must take into account the coefficient of expansion of the two modifications. This correction, which is of course uncertain since the experimental results of BELLATI and ROMANESE differ widely from those of BEHN, we have calculated from the data given by the latter author, since these inspire the greater confidence when considered in conjunction with BRIDGMAN's measurements ¹⁾.

We obtain:

$$(v_{IV})_{32^{\circ}.3} = 0.58250 + 0.58250 \times 0.3 \times 0.00048 = 0.5826$$

$$(v_{III})_{32^{\circ}.3} = 0.60465 - 0.60465 \times 0.2 \times 0.00036 = 0.6046.$$

Then: $(v_{III} - v_{IV})_{32^{\circ}.3} = 0.0220 \frac{cc.}{gm.}$

¹⁾ Proc. Americ. Acad. of Arts and Sciences, 51, 581 (1916); especially p. 617.

TABLE V.

| $c = 2.410; \quad v_c = 0.75064;$ | | $c = 2.426; \quad v_c = 0.75024$ | | | | |
|------------------------------------|--------------------------|----------------------------------|-----------------------|---------|---------|---------|
| Number of experiment \rightarrow | Temperature 32° 00 C. | | Temperature 32° 50 C. | | | |
| | 7 | 9 | 3 | 6 | 7 | 9 |
| m_1 | 26.8885 | 25.5881 | 26.2907 | 25.3082 | 26.8885 | 25.5881 |
| $m_2 - m_1$ | 2.5396 | 3.2543 | 2.8089 | 3.3314 | 2.5401 | 3.2547 |
| $(m_2 - m_1)c$ | 6.1203 | 7.8427 | 6.8147 | 8.0823 | 6.1625 | 7.8962 |
| $(m_2 - m_1)(1 + c)$ | 8.6599 | 11.0970 | 9.6236 | 11.4137 | 8.7026 | 11.1509 |
| $m_1 - (m_2 - m_1)c$ | 20.7682 | 17.7454 | 19.4760 | 17.2259 | 20.7260 | 17.6919 |
| V | 18.5974 | 18.6677 | 18.9956 | 18.9798 | 19.0579 | 19.0662 |
| $(1 + c)(m_2 - m_1)v_c$ | 6.5005 | 8.3298 | 7.2200 | 8.5631 | 6.5291 | 8.3659 |
| $V - (1 + c)(m_2 - m_1)v_c$ | 12.0969 | 10.3379 | 11.7755 | 10.4167 | 12.5288 | 10.7003 |
| v_s | 0.58248 | 0.58251 | 0.60460 | 0.60470 | 0.60449 | 0.60481 |
| | Mean: 0.58250 | | Mean: 0.60465 | | | |

C. *Second Method for the Determination of $(v_{III} - v_{IV})$.*

16. This is simpler than the first method, and since the hitherto uncertain correction discussed above does not have to be applied here, this method gives us the value of $v_{III} - v_{IV}$ with greater accuracy.

An exactly determined weight of the dry salt in the form of the modification IV is placed in the bulb of a dilatometer, this is filled with a liquid in which the salt is practically insoluble, and a capillary is joined on to the bulb. One can also previously saturate the liquid used with the salt. We used toluene. After the air is removed from the apparatus by careful warming (in this process the transition temperature must not be exceeded) and evacuating, a porcelain scale graduated in millimeters is fixed behind the capillary and the instrument is immersed in the water in a thermostat which is kept at the transition temperature for some days. Now and then the position of the meniscus (S_1) in the capillary is observed.

When the latter no longer alters, the thermostat is brought to a temperature which lies a few degrees above the transition temperature, so that IV is transformed completely into III. The velocity of transformation is so great at 36°, that the process is complete at the end of about an hour. One makes certain that the position of the meniscus does not change; then the temperature of the thermostat

is brought back again to $32^{\circ}.3$. When now the position of the meniscus no longer changes (this is sometimes observed for several days, though one gets the impression that a few hours suffice) the position (S_2) is noted. Then we determine the volume of the capillary between S_1 and S_2 at $32^{\circ}.3$ by filling this portion with mercury and weighing the latter. Thus we obtain the required volume-change $v_{III}-v_{IV}$ at the inversion temperature.

In this method of working one is completely independent of the question whether the capillary tube is cylindrical between S_1 and S_2 .

Care must be taken accordingly that the capillary tube is completely immersed in the water of the thermostat whilst determining the points S_1 and S_2 . If the temperature of the tube is different from that of the water, this must be brought into the calculation.

17. We have carried out four determinations: one using 24.2815 gm. of the salt, three with 22.3699 gm. in a second dilatometer the capillary of which was narrower. Table VI gives the results.

The capillary of the first dilatometer contained 6.9151 gm. of mercury in 180 mm., that of the second dilatometer 6.7656 gm. in 300 mm. Both weighings refer to the transition-temperature.

Special measurements made for this purpose established that the temperature-variations of the thermostat ($0^{\circ}.01$) can be ignored here, since the movement of the toluene meniscus in this temperature-interval was only 0.08 mm.

TABLE VI.
Temperature $32^{\circ}.3$ C.

| First Dilatometer. Weight of salt 24.2815 gm. | | | | Second Dilatometer. Weight of salt 22.3699 gm. | | | |
|--|---|-----------------------|---------------------------------|---|---|-----------------------|---------------------------------|
| Meniscus at start of experiment. | Meniscus at end of experiment. | Displace- ment mm. | Volume change cc. per gm. | Meniscus at start of experiment. | Meniscus at end of experiment. | Displace- ment mm. | Volume change cc. per gm. |
| 19.6 | 208.0 | 188.4 | 0.0220 ^s | 31.7 | 324.0 | 296.4 | 0.0221 ¹ |
| | | | | 19.3 | 318.7 | 299.4 | 0.0223 ^s |
| | | | | 19.3 | 316.0 | 296.7 | 0.0221 ^s |

For the mean of all we obtain:

$$(v_{III}-v_{IV})_{32.3^{\circ}} = 0.0221^s \frac{\text{cc.}}{\text{gm.}}$$

For the reasons given above § 15 we believe that this value is more reliable than that determined by the first method.

18. When our investigation was already completed we found that the paper of BEHN quoted above contained data which put us in a position to calculate $(v_{\text{III}} - v_{\text{IV}})$ for the transition temperature assigned by him of 32° . As indicated above (§ 6) we find:

$$(v_{\text{III}} - v_{\text{IV}})_{32^\circ.0} = 0.022 \frac{\text{cc.}}{\text{gm.}}$$

19. It may perhaps turn out later to be necessary (in connection with another investigation on which we are engaged) to determine $(v_{\text{III}} - v_{\text{IV}})$ at the transition temperature with greater accuracy. But so much is certain at present, that the value found by BRIDGMAN is about 9 per cent too low.

20. If column 3 of our Table I be examined more closely, the regular increase of $(v_{\text{III}} - v_{\text{IV}})$ with equal increments of pressure is noticeable, though at the highest pressure (800 Kg/cm^2), $(v_{\text{III}} - v_{\text{IV}})$ has not yet reached the value which we found for 1 atmosphere.

One gets the impression that in BRIDGMAN's experiments (also in those under pressure) only a definite fraction of the whole mass of the ammonium nitrate taken has actually been concerned in the transformation. That this has actually been the case will seem very probable, when BRIDGMAN's¹⁾ words are read: "Two series of runs were made, separated by an interval of a year. For each of these series of runs the material was hammered dry into a perforated steel shell, and the pressure transmitted directly to it by kerosene. For the second run, the salt was subjected to a preliminary drying in vacuum at 100° . No difference in behavior between the two runs to be attributed to this cause was to be detected. The second series, repeating the first, was made necessary by the fact that the measurements of $\Delta v (= v_{\text{III}} - v_{\text{IV}})$ given by the first series were irregular. The reason for this is that ammonium nitrate is a substance for which it is particularly difficult to force the reaction from one phase to another to run to completion".

Apparently in the "first run" there are always parts of the whole mass of salt which have *not* suffered the transformation, while in the "second run" (at all pressures) a definite portion plays *no* part

¹⁾ Proc. Americ. Acad. of Arts and Sciences 51, 581 (1916); especially p. 605.

in the change. The last appears very probable when we consider the method according to which the experiment was carried out. For if the salt were hammered into the steel container mentioned in portions, it is quite possible that one such block may take part *throughout* in the change, whilst a second, which had been hammered down on top of it, did *not*, although the contact between the two blocks left nothing to be desired.

Investigations, undertaken by ERNST COHEN and A. L. TH. MOESVELD ¹⁾ some years ago and continued to the present day, provide an illustration of what has been said here. If a warm saturated aqueous solution of thallium picrate is cooled below the temperature of

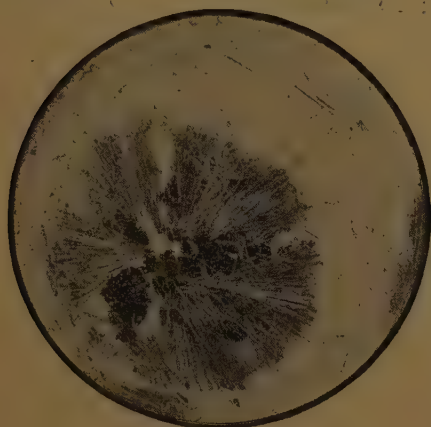


Fig. 3.

inversion (46°) of this salt, the red modification of which undergoes changes at that temperature into the yellow form (the red is stable below 46°), both forms crystallise close together, and are existing in contact with the solution and with one another for months. If the water is evaporated, there is obtained a mixture of the two modifications, although there is close contact between the red and yellow crystals. There is in our possession a mixture of this kind which has already been four years in this state; it was preserved at 15° C., therefore thirty degrees below the temperature of inversion. In Fig. 3, a photographic reproduction of this preparation, the difference between the two modifications is clearly distinguishable, although the colour-difference (red and yellow) cannot be exhibited.

21. The suspicion arises that similar phenomena may have played a part with the other substances investigated by BRIDGMAN. In fact he himself mentions that the reluctance discussed here was observed by him in many substances. Accordingly, the figures which he found for the corresponding volume-change and for the heat of transformation calculated from these would become of dubious value. A repetition of the experiments in question appears therefore to be necessary. We hope to return to this later.

¹⁾ Zeitschr. f. physik. Chemie **94**, 450 (1920).

S U M M A R Y.

It has been shown that BRIDGMAN's determinations of the volume-change which takes place when ammonium nitrate IV is transformed into the modification III, contain an error of about 9 per cent, as the result of the obstinate reluctance to undergo this change which can be observed. Now quantitative evidence is thereby offered that the physical constants of many substances which we know at present, often refer to metastable mixtures of the modifications of those substances, of unknown composition.

A real meaning can only be assigned to these constants when they have been determined for the pure modifications.

Utrecht, December 1923.

VAN 'T HOFF-*Laboratorium.*

Chemistry. "*The Metastability of the Elements and chemical Compounds in consequence of Enantiotropy or Monotropy*". V. By Prof. ERNST COHEN and A. L. TH. MOESVELD.

(Communicated at the meeting of December 29, 1923).

1. In the several cases which we discussed from a qualitative and quantitative point of view in our earlier publications under the above title, it was shown that those solid substances with which we are accustomed to deal daily in the laboratory, are mixtures of the possible modifications in which such substances may exist. Accordingly, no significance can be attached to their physical constants as hitherto determined. In those experiments which we described in our previous publication it was shown that these constants were liable to great errors, (e.g. 10%), when determinations were carried out with these mixtures rather than with the pure modifications. In addition to other methods the more recent physical methods involving the use of *X*-rays make it possible for us to ascertain whether any single substance is really a mixture of different modifications or not. Such methods should be used previous to the determinations of the physical constants of such a substance.

2. The following example may serve to show how necessary it is to account for the observed facts when dealing with mixtures in cases where no particular precautions were employed to separate the pure modifications of a certain substance. In the case of an *X*-ray analysis of silver iodide WILSEY¹⁾ found that this salt (investigated by the powder method of DEBYE and SCHERRER) crystallized in the cubic form. This result was confirmed by DAVEY²⁾. Shortly afterwards, however, doubt was thrown on the correctness of this result by AMINOFF³⁾, who in the meantime had concluded from his own experiments that silver iodide was hexagonal. In his "Survey of existing crystal structure data" WYCKOFF⁴⁾ supports AMINOFF's conclusions, and agrees that his own results — not yet completed — point to the necessity of attributing a hexagonal structure to silver

¹⁾ Phil. Mag. (6) 42, 262 (1921).

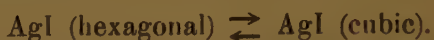
²⁾ Phys. Rev. 19, 248 (1922).

³⁾ Geol. För. Forh. 44, 444 (1922); Physik. Ber. 1922, p. 827.

⁴⁾ Journ. Franklin Inst. 195, 183, 349, 531 (1923).

iodide. That a cubic structure should ever have been assigned to it calls forth the following remarks from his pen: "Silver iodide is particularly interesting because in the ease with which it was assigned a cubic structure, though possessed of hexagonal symmetry, it furnishes an excellent illustration of the insufficiency of unaided powder photographs, and sounds a warning of the dangers arising from a disregard of available crystallographic information".

3. It has been known for a long time that silver iodide is polymorphous; at atmospheric pressure it gives evidence of a transition temperature at 146° .



In consideration of our earlier communications we must expect that, when no special precautions are taken, we may have to deal at ordinary temperatures, with a mixture of the metastable cubic and the stable hexagonal forms of the iodide. The result obtained by WILSEY¹⁾ is therefore in perfect agreement with this, as may be seen from the following. "The conclusion is that both crystal forms exist, most of the samples showing a mixture of the two in which the hexagonal form predominates. The discrepancies in the results reported by different observers appear to be due to differences in the samples examined rather than in the methods of analysis used", and further: "The evidence appears quite conclusive that every sample of silver iodide studied contained the cubic form; in a few cases none but the cubic structure was evident, in some, one or two faint lines were present which belonged only to the hexagonal form; while in most of the samples the hexagonal form predominated".

4. Although WILSEY did not make a systematic investigation of the conditions under which either one or other of these modifications exists, he nevertheless observes that the first product exhibiting the cubic form was prepared by precipitation. The other cubic crystals were obtained by melting the salt and subsequently chilling in cold water; while at the same time the very prominent hexagonal crystals were almost always formed whether in the case of chilling or slower cooling of the molten salt respectively, or by precipitation. Here too then, we find extending in every direction the predictions of our earlier work. From the above remarks it follows likewise that the quotation of WYCKOFF cited in § 2 loses its significance, at least in so far as silver iodide is concerned.

Utrecht, December 1923.

VAN 'T HOFF-Laboratorium.

¹⁾ Phil. Mag. (6) 46, 487 (1923).

Chemistry. — "*The decomposition of Cottonseed-Oil in a Closed Vessel at 450° Compared with the Hydrogenation of this Oil by the Method of BERGIUS with Hydrogen under High Pressure.*"
By Prof. H. I. WATERMAN and J. N. J. PERQUIN. (Communicated by Prof. J. BÖESEKEN.)

(Communicated at the meeting of September 29, 1923).

A. MAILHE recently carried out some experiments on the preparation of mixtures of hydrocarbons from fats.¹⁾ MAILHE made use of catalysts and from different kinds of vegetable oils he obtained at 600°—650° gases of high calorific value, which contained H₂, CO, and CO₂, and lower hydrocarbons, a liquid of low boiling-point, and a distillation residue. By subjecting the latter once more to the same treatment, he finally obtained only gases and a low-boiling liquid as a final-product. This liquid still contained some acid; it was neutralized with lye, and then hydrogenated over metal at 180°—200°. Thus MAILHE obtained hydrocarbon mixtures, consisting of saturated and aromatic hydrocarbons, and also of naphthenes. This treatment was applied to different vegetable oils. For the way in which the reaction takes place, as MAILHE imagines it, we may refer to his publication²⁾.

Industrially these researches are of no importance excepted of course under abnormal conditions which may possible arise in different countries from time to time. Formerly ENGLER³⁾ has prepared during his classical research these hydrocarbon mixtures in a still simpler way. He obtained by distillation of fish oil at 300°—400° and 4—10 atmospheres about 75 % of a liquid mixture of hydrocarbons.

In this investigation of ENGLER's it was particularly of great importance that the process of conversion takes place almost quantitatively. Here too there were formed besides the *liquid* hydrocarbons, also *gaseous* ones, chiefly CH₄, but further also CO, CO₂, and water.

Investigations made by us of late concerning BERGIUS' hydrogenation process induced us to extend this research also to fats.

¹⁾ Préparation de pétrole à l'aide d'huiles végétales et animales, Bulletin de la Société de Chimie Industrielle 4, 40 (Octobre 1922); La pyrogénéation catalytique des huiles animales, La revue pétrolifère, 1, N^o 17, Mars 17, 1923.

²⁾ Compare also Katalyse und Erdölbildung, C. ENGLER, Chemie und Physik des Erdöls, Leipzig 1913, p. 412 et seq.

³⁾ C. ENGLER—H. HÖFER, Das Erdöl II, 110 (1909).

In the berginisation of products containing carbon and hydrogen one has only to deal with two processes, the process of cracking and the process of hydrogenation; in this case, however, the matter was still somewhat more complicated, because here the hydrocarbons must first be formed from fats. It is self-evident that here the berginisation experiment proper had to be compared with the cracking experiment.¹⁾ Where in his distillation experiments ENGLER worked at 300° and 400° and under a comparatively low pressure, this experiment was carried out at much higher temperature (450°) and very high pressure.

For the rest the way of experimenting was analogous to that followed by us with paraffine as experimental material²⁾. Only with this difference that here a high-pressure apparatus constructed for the purpose was used (see figure 1)³⁾. Besides, the temperature in the metal wall of the autoclave was measured, by which it was ascertained during the experiments that there was no question of any overheating of the walls. The capacity of the autoclave was $\pm 1.000 \text{ cm}^3$. In the experiments described here no use was made of the condenser.

Both experiments are recorded in table A.

It has been proved by the experiments that also under these circumstances the fatty oils are converted into mineral oil to a very great percentage, just as this is the case in ENGLER's experiments.

It is clear from the graphical representations fig. 2, in which the change of pressure and temperature is given, how very sensitive the apparatus used is, and how accurate the results obtained are. Even very small variations of temperature are immediately expressed in the pressure-curve. The change of the pressure during the berginisation is essentially different from that in the cracking experiment. The rise of the pressure is considerably smaller in the berginisation than in the cracking.

Furthermore it appears from the gas-analysis that the oxygen of the cottonseed oil is driven out in both cases almost quantitatively as CO , CO_2 , and H_2O . Smaller quantities of acids (compare acid percentage) and ketones may still be present in the oil obtained. The

¹⁾ The decomposition when cottonseed oil is heated in a closed vessel is always called "cracking" in what follows.

²⁾ H. I. WATERMAN and J. N. J. PERQUIN, Hydrogenation of paraffin by the BERGIUS's Method; Proceedings Kon. Akad. v. Wetensch., Amsterdam, Vol. XXVI, 226 (1923).

³⁾ In the construction of this apparatus we had the assistance of Prof. J. C. ANDRIJSEN, for which we express our thanks to him here.

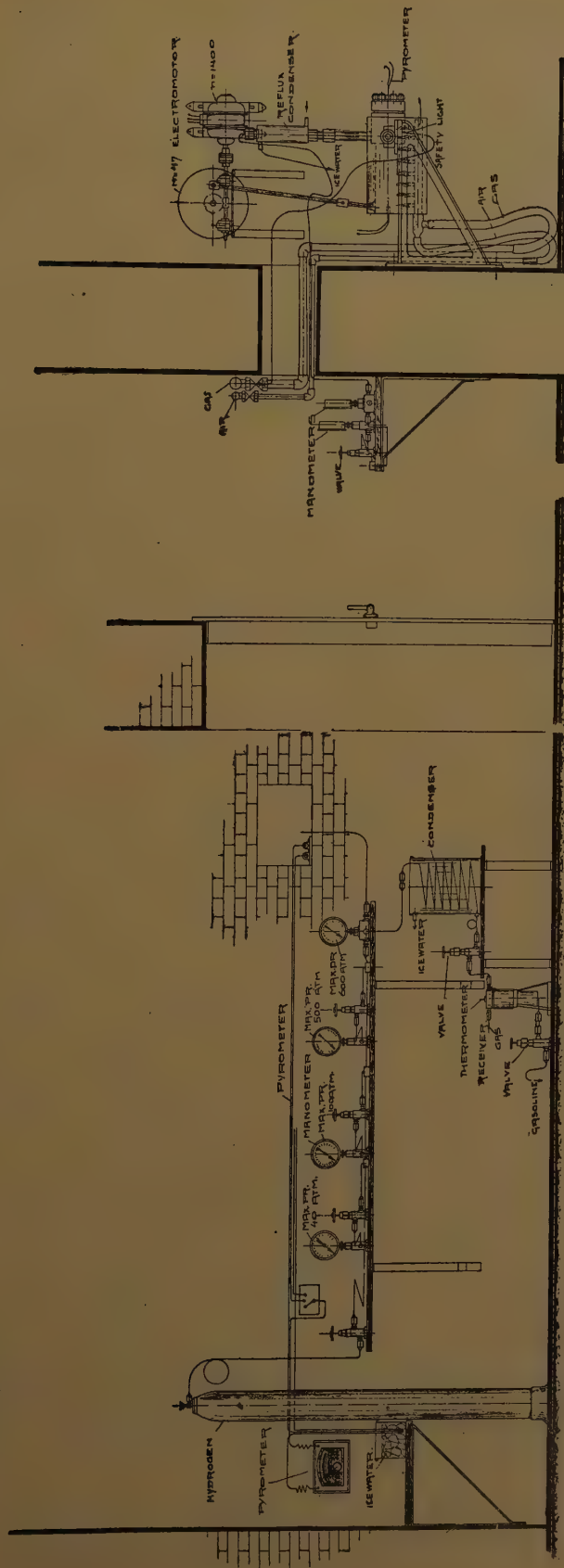
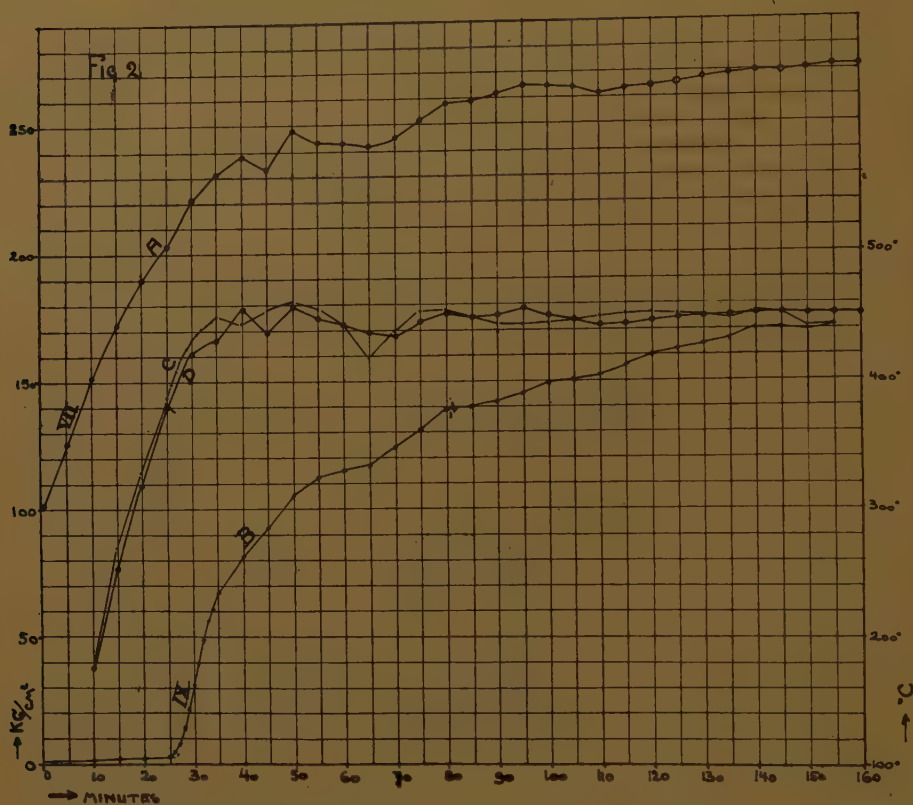


Fig. 1.

expulsion of the oxygen from the oil is very clearly shown by the oxygen balance.

If it was already very probable from the shape of the pressure curve that hydrogenation really took place in the berginisation, this appeared with certainty from the gas analysis. Considerable quantities of hydrogen have been consumed.



A and B: PRESSURE CURVES

C: TEMPERATURE CURVE IX

D: TEMPERATURE CURVE VII

| Oxygen balance | | | |
|---------------------------------|----------|---|----------|
| Experiment N ^o . VII | | | |
| Before the experiment | | After the experiment | |
| In cottonseed oil | 32.4 gr. | In gases: ¹⁾ CO ₂ | 20.5 gr. |
| In hydrogen | | CO | |
| (O ₂ content: 2.0 %) | 2.2 gr. | O ₂ | |
| | 34.6 gr. | In water (10 gr.) | 8.9 gr. |
| | | Total | 29.4 gr. |

¹⁾ Leaving water vapour out of consideration.

| Oxygen balance | | | |
|-----------------------|----------|---|----------|
| Experiment No. IX | | | |
| Before the experiment | | After the experiment | |
| In cottonseed oil | 32.4 gr. | In gases: ¹⁾ $\left. \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \end{array} \right\}$ | 22 gr. |
| | | In water (2 gr.) | 1.8 gr. |
| | | Total | 23.8 gr. |

¹⁾ Leaving water vapour out of consideration.

We have set ourselves the question already before ¹⁾, in how far, also in the ordinary cracking experiments the hydrogenation in BERGIUS' sense may take place to a smaller or greater degree. This hydrogenation is called by us internal hydrogenation in contrast with that which is brought about by the hydrogen supplied from the outside. It might be possible that also in this cracking experiment internal hydrogenation has taken place. In this case there is, however, another way possible, namely that in which the CO formed during the process by the action on water, might yield hydrogen in statu nascendi: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$.

At the time ENGLER and GRIMM already drew attention to the hydrogenation by means of carbon monoxide²⁾, FISCHER and SCHRADER have systematically investigated the hydrogenation of coal with carbon monoxide³⁾. Whether the internal hydrogenation and the indirect hydrogenation by CO in such experiments as performed by us, actually takes place, and if so to what degree, will have to appear in a separate investigation.

The indirect hydrogenation by CO can, indeed, also have taken place in the berginisation experiment, though there, in consequence of the excess of hydrogen, the watergas equilibrium will shift to the side of the CO.

In both experiments the losses were important, the loss being greatest in the cracking experiment. This is perhaps partly caused by condensation of hydrocarbons and water in the tubes between the manometers and the autoclave; there were also losses during

¹⁾ Congrès international des combustibles liquides. Paris 9—15 Octobre 1922, Chimie et Industrie, Mai 1923, p. 200—207.

²⁾ Compare ENGLER und J. GRIMM, Ueber direkte Abspaltung von Kohlenoxyd und die Umsetzung desselben mit Wasser. Berichte 30, 2925—26 (1897).

³⁾ Compare FR. FISCHER und H. SCHRADER, Hydrierung von Kohlen durch Kohlenoxyd. Brennstoffchemie 2, 257 (1921).

| No. of the experiment | Time of heating to the required temperature. (in minutes) | Duration of the experiment proper (in minutes) | Initial pressure in atmospheres | Maximum pressure in atmospheres | Final pressure in atmospheres | 298 gr. cottonseed oil used obtained in gr. resp. in percentage of weight | | | | | Oil | | |
|--|--|---|-----------------------------------|---------------------------------|-------------------------------|---|--------------|----------------|---------------|---------------|-----------------------------|------------|------------------------------|
| | | | | | | oil | water | gas | coke | loss | Sp. gr. at $\pm 15^{\circ}$ | Acid value | D. En- cer Gasoline to |
| VII | 40 | 120 | 101 | 272 | 47,7 | 203 (66,0 %) | 10 (3,3) | 68 (22,3) | 5,5 (1,8) | 20,3 (6,6) | 0,793 | 5,1 | 60 (44,) |
| IX | 35 | 120 | 0 atmos- pheric pressure | 171 | 32,0 | 169 (56,7 %) | 2 (0,7) | 64 (21,5) | 15 (5,0) | 48 (16,1) | 0,818 | 1,0 | 5 (35,) |
| Used ± 200 Gr. cottonseedoil (XXII : 200 Gr., XXIII : 204 Gr., XXIV : 200 Gr., XXV : 198 Gr., XXVI : 202 Gr., XXVII : 201 Gr.); obtained from this in gr. | | | | | | | | | | | | | |
| | | | | | | oil | water | gas | coke | loss | | | |
| XXII ¹⁾ | 35 | 60 | 110 | 270 | 79 | 126 (59,3 %) | 8,5 (3,9) | 69 (32,4) | 1 (0,5) | 8,9 (3,9) | 0,774 | 0,3 | 67, (43, |
| XXIII | 35 | 60 | 110 | 251 | 85 | 146 (67,2 %) | 8,5 (3,9) | 58 (26,7) | 0,6 (0,3) | 4,3 (1,9) | 0,790 | 7,6 | 59, (43, |
| XXIV ²⁾ | 35 | 60 | 0 | 79,5 | 22 | 124 (62 %) | 1 (0,5) | 42 (21) | 14 (7) | 19 (9,5) | 0,817 | 1,3 | 52, (35, |
| XXV | 33 | 60 | 0 | 81,5 | 21,6 | 132 (66,6 %) | 3,5 (1,7) | 44 (22,2) | 14 (7,1) | 4,5 (2,3) | 0,812 | 1,9 | 55, (38, |
| XXVI | 40 | 60 | 0 | 81,5 | 21,5 | 127 (63 %) | 3,5 (1,7) | 46 (22,8) | 14,5 (7,2) | 11 (5,5) | 0,816 | 2,3 | 55, (37, |
| XXVII | 36 | 5 | 110 | 222 | 96,5 | 172 (81,4 %) | 9,5 (4,5) | 30,8 (14,6) | 0,6 (0,3) | — — | 0,847 | 36,4 | 19, (17, |

- ¹⁾ The thermo-couple having been slid from the tube, the temperature rose in this
- ²⁾ Just before the termination of this experiment there arose a small leakage, which co
- ³⁾ The figures placed between brackets indicate the yield in percentages of weight
- ⁴⁾ Gasoline inclusive the loss in the distillation by ENGLER's method.
- ⁵⁾ The percentages placed between brackets have been calculated on gas free from
- ⁶⁾ Determined experimentally.

TONSEED OIL AT 450°.

| Loss. | Bromine value (addition) of the | | Acid value of the | | Gases obtained: | | | | | | | | | Number of litres of supplied hydrogen | Number of litres of hydrogen still present | Number of litres of hydrogen consumed | Absorbed hydrogen in grammes | Percentages of weight of hydrogen absorbed |
|-------|---------------------------------------|----------|----------------------|----------|--------------------|------------------------------|-----------------|-------------------------|----------------|----------------|----------------|-------------------------|--------------------|--|---|--|---------------------------------|---|
| | Gasoline | Kerosene | Gasoline | Kerosene | Quantity in litres | Density compared with air | Analysis 5) | | | | | | | | | | | |
| | | | | | | | CO ₂ | Heavy hydro- carbons | O ₂ | CO | H ₂ | Other hydro- carbons | (rest) Nitrogen | | | | | |
| 5,2 | 14,5 | 6,5 | 3,2 | 0,9 | 63 | 0,877 | 18,8 (24,4) | 1,1 (1,4) | 0,4 (0,5) | 7,3 (9,5) | 23,0 | 44,2 | 5,2 | ± 75 L. (8,8 Gr.) | 14,5 | 60,5 | 5,4 | 1,8 |
| 5,0 | 16,8 | 8,5 | 0,3 | 1,8 | 51 | 1,022 | 23,8 (25,9) | 2,8 (3,0) | 0,9 (1,0) | 10,9 (11,8) | 8,0 | 49,9 | 3,7 | | | | | |
| | | | | | | | | | | | | | | | | | | |
| 6,4 | 17,2 | 5,2 | 0,3 | 0,1 | 95 | 0,582 | 8,5 (18,4) | 0,4 (0,9) | 0,4 (0,9) | 6,2 (13,4) | 53,9 | 27,1 | 3,5 | 108 L. 6) (13,4 Gr.) | 51,2 | 56,8 | 5,1 | 2,5 |
| 4,8 | 17,0 | 5,0 | 6,3 | 1,2 | 92 | 0,512 | 9,3 (24,3) | 1,0 (2,6) | 0,5 (1,3) | 3,7 (9,7) | 61,8 | 20,0 | 3,7 | 108 L. 6) (13,4 Gr.) | 57,0 | 51 | 4,6 | 2,3 |
| 3,6 | 24,3 | 7,9 | 1,0 | 0,2 | 31 | 1,094 | 27,9 (31,2) | 4,8 (5,4) | 0,9 (1,0) | 10,0 (11,1) | 10,5 | 45,8 | | | | | | |
| 2,3 | 24,0 | 7,9 | 1,9 | 0,3 | 32,5 | 1,077 | 26,4 (29,4) | 4,6 (5,1) | 1,1 (1,2) | 12,8 (14,2) | 10,3 | 38,2 | 6,6 | | | | | |
| 4,0 | 24,0 | 7,6 | 2,4 | 0,4 | 33,5 | 1,093 | 25,4 (28,2) | 4,2 (4,7) | 0,8 (0,9) | 13,4 (14,9) | 10,0 | 40,8 | 5,4 | | | | | |
| 1,7 | 42,0 | 15,6 | 22,7 | 7,6 | 103 | 0,239 | 5,0 (33,3) | 0,4 (2,7) | 0,3 (2,0) | 2,9 (19,3) | 85,0 | 6,4 | | 111,4 L. 6) (10,0 Gr.) | 87,5 | 23,9 | 2,1 | 1,0 |

g the last 10 minutes to ± 500°.
ired by screwing on the reflux cooler.
duct.

the opening and pouring out. In a series of observations made later (berginisation experiments XXII and XXIII and cracking experiments XXIV, XXV and XXVI) the results of which are likewise recorded in table B, we have succeeded in reducing these losses greatly by placing a reflux cooler on the autoclave. The oxygen balances are in still better harmony there.

| Oxygen balance | | | |
|--|----------|---|----------|
| Experiment N ^o . XXII | | | |
| Before the experiment | | After the experiment | |
| In cottonseed oil | 21.7 Gr. | In gases: ¹⁾ $\left. \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \end{array} \right\}$ | 16.3 Gr. |
| In supplied hydrogen (O ₂ content 2.5 %) | 3.9 Gr. | In water | 7.5 Gr. |
| Total | 25.6 Gr. | Total | 23.8 Gr. |

¹⁾ Leaving watervapour out of consideration.

| Oxygen balance | | | |
|---------------------------------|----------|---|----------|
| Experiment N ^o . XXV | | | |
| Before the experiment | | After the experiment | |
| In cottonseed oil | 21.5 Gr. | In gases: ¹⁾ $\left. \begin{array}{l} \text{CO}_2 \\ \text{CO} \\ \text{O}_2 \end{array} \right\}$ | 15.7 Gr. |
| | | In water | 3.1 Gr. |
| | | Total | 18.8 Gr. |

¹⁾ Leaving watervapour out of consideration.

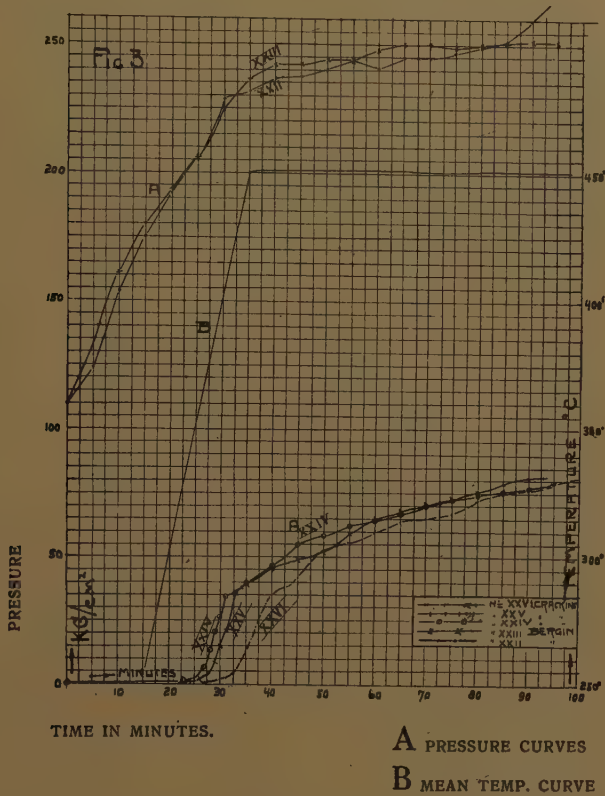
Fig. 3 represents the change of pressure and temperature in these experiments. The experiments were always made with about 200 gr. of cottonseed oil. For the rest the circumstances were analogous to those of nrs. VII and IX.

It may be a drawback for the technical execution of these experiments that the iron of the apparatus is pretty quickly attacked through the formation of organic acids.

It appears from the experiments described that both by cracking and by berginisation, cottonseed oil can very efficiently be converted into hydrocarbon mixtures with high gasoline percentage. It appears from experiment XXVII, which was heated for 36 minutes, and was kept at a temperature of 450° for only 5 minutes, that even after this short period of heating a considerable part of the oxygen of the fat had been

expelled, while the hydrocarbons formed also had been partially decomposed, so that a considerable yield of gasoline and kerosene had been obtained already.

The conversion is not yet complete here, as appears among other things from the high acid value (36,4) of the oil.



The value of unsaturation (bromine value) of the gasoline and kerosene formed is greater in XXVII than in the other berginisation experiments. In all these experiments the behaviour of the cottonseed oil is not very different from that of a hydrocarbon mixture, as the oxygen can easily be eliminated from it. In the berginisation of the cottonseed oil very much hydrogen is consumed, among others directly or indirectly for the formation of water. In both processes formation of coke takes place, this being considerably less in the berginisation experiments. We have been struck with the fact that also in other berginisation experiments with paraffine, formation of small quantities of "carbon" takes place. It will be of great importance to perform a berginisation experiment in which this separation of carbon is entirely absent. If this does not succeed, it will have to be examined

in how far this carbon, which has been formed during the process, and which will be active according to CHANEY¹), at least if it is formed at low temperature (below 500°—600° C.), may act as a catalyst²).

In conclusion we express our thanks to Mr. J. A. BEUKERS, who has assisted us in the execution of an important part of these observations.

Delft.

*Laboratory of Chemical Technology
of the Technical University.*

¹) N. K. CHANEY, The activation of carbon, Transactions of the American electrochemical Society, **36**, (1920).

²) A similar investigation should also be carried out with regard to metals that are accidentally present, as nickel, vanadium etc. Compare RAMSAY, J. of the Soc. of Chem. Ind. **42**, p. 287 T. (1923).

Mathematics. — “On a metric theorem of CARATHÉODORY”. By Prof. J. WOLFF. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of November 24, 1923).

1. In a space of an arbitrary number of dimensions we suppose a right angled system of coordinates. We call two points P and Q *congruent*, if the vector PQ has rational components. The points congruent with the origin O are the rational points.

2. A set of points E without a congruent pair of points is *im-measurable* or has the *measure zero*.

Without detracting from the generality we suppose E to be limited. We suppose the exterior measure μ^*E of E to be positive and we shall show that the interior measure μ_*E is zero.

Let $R_0 = 0$, R_1, R_2, \dots be the set of the rational points of which the distances to O are less than 1. The vectors OR_n we call q_n . The set arising from E by the translation q_n we call E_n . In particular $E_0 = E$. The E_n have equal interior measures μ_*E and equal exterior measures μ^*E . If $m \neq n$, E_m and E_n have no point in common. For a common point P would get into E by the translation $-q_n$ as well as by the translation $-q_m$, and these two points of E must coincide as E does not contain a congruent pair of points; hence $q_m = q_n$, $m = n$.

We consider the set

$$S = E_0 + E_1 + \dots$$

S is limited, hence

$$\mu_*S < \infty \quad (1)$$

As no two E_n have any points in common

$$\mu_*S \leq \sum_{n=0}^{\infty} \mu_*E_n \quad (2)$$

As each $\mu_*E_n = \mu_*E$, it follows from (1) and (2) that

$$\mu_*E = 0.$$

3. In the same way the following theorem is proved:

Let there be chosen an arbitrary enumerable infinite limited set of points (A_n) . Each measurable set with positive measure contains one pair of points the joining vector of which is equal to a vector $A_m A_n$.

4. Let E be a measurable set of points of which the measure $\mu E > 0$. To each point P of E we associate the set of the points of E that are congruent with P (see 1). In each of these sets we choose a point. *The set E_0 of the chosen points is immeasurable.*

Without loss of generality we suppose the diameter of E to be less than 1. From E_0 we derive the sets E_n by means of the translations mentioned in § 2. No two of these E_n have any point in common. If we put again:

$$S = E_0 + E_1 + \dots,$$

S is limited, so that we find just as in § 2.

$$\mu_* E_0 = 0 \quad \dots \quad (3)$$

S contains E , for each point of E is congruent with a point of E_0 and has a distance < 1 from this point.

Hence

$$\mu^* E \leq \mu^* S \leq \sum_{n=0}^{\infty} \mu^* E_n \quad \dots \quad (4)$$

As $\mu^* E > 0$ and each $\mu^* E_n = \mu^* E_0$, we have

$$\mu^* E_0 > 0 \quad \dots \quad (5)$$

From (3) and (5) it follows that E_0 is immeasurable and in this way we have simplified the proof of the theorem given by CARATHÉODORY¹⁾ that every measurable set with positive measure has immeasurable parts.

Utrecht, Nov. 1, 1923.

¹⁾ C. CARATHÉODORY, Vorlesungen über reelle Funktionen, 1918, p. 349 sqq.

of length $\frac{1}{(0!)^0} = 1$, in the middle of the two remaining segments an interval of length $\frac{1}{(1!)^1}$, in the middle of each of the 2^2 remaining segments an interval of length $\frac{1}{(2!)^2}$ etc. Let P be the perfect set that has the set of intervals, constructed in this way, for complement. The distance of each pair of points of P that are not the endpoints of a complementary interval, is irrational, for according to (1) and the construction P has the measure zero, so that the distance of such a pair of points is a number B . Hence any perfect part of the sets which remains after emission from P of the end points of the complementary intervals, has the property in question.

Utrecht, December 1, 1923.

Physios. — “*On the cristalstructure of white tin*”. By A. E. VAN ARKEL.
(Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of February 24, 1923).

Continuing the research of Dr. BURGER¹⁾ on the properties of single-crystal-wires of tin, Röntgenograms were taken to determine the orientation of the crystals in relation with the axis of the filament. The results of this determination were not in agreement with the conclusions arrived at by BIJL and KOLKMEIJER²⁾.

These authors found that the elementary cell of tetragonal tin contains three atoms, one of them forming the corners of the tetragonal prisma, whilst the other two are placed in the centers of the four equivalent sides.

As the structure-factor³⁾, by which the intensities are to be multiplied in this case is 9, when all indices of the reflecting spaces are either even or odd, and unity in all other cases, all faces will reflect in first order. Reflection-lines of all possible crystallographic faces therefore must be present, in any case those with small indices, as these for several reasons have a greater intensity.

Now on BIJL's films the reflections from the (100) and (110) faces are absent, whereas the reflection of (101) as BIJL indicates, is present. The reflection (310), also fails, whereas the reflection (410) which theoretically should be equally strong, is present.

Therefore there is some doubt whether the structure, as proposed by BIJL, is the true one.

In table I the values of $\sin^2 \frac{\theta}{2}$ are put together: (1°) as mentioned by BIJL, (2°) those given by JOHNSON⁴⁾ and (3°) the mean of six films taken in this laboratory, partly by Dr. BURGER; also (4°) the relative intensities, as they should be according to the structure, proposed by BIJL and (5°) the estimation by the same author. The

¹⁾ H. C. BURGER. *Physica* 2, 56 (1922).

²⁾ A. J. BIJL and N. H. KOLKMEIJER. *Proc. Roy. Soc. A'dam.* 21, 501 (1919).
A. J. BIJL. *Diss.* Utrecht 1918.

³⁾ See a.o. DEBIJE and SCHERRER. *Physik. Zeitschr.* 18, 298 (1917).

⁴⁾ BIJL indicates only those lines, that are *not* in agreement with his own measurements.

mean error of position in our measurements is about 0.3%, except for the first lines. The position of the lines agrees fairly well with the other values, especially with those of JOHNSON.

TABLE I.

| Intensity | | $\sin^2 \frac{\Theta}{2} \times 10^3$ | $\sin^2 \frac{\Theta}{2} \times 10^3$ | $\sin^2 \frac{\Theta}{2} \times 10^3$ | $\sin^2 \frac{\Theta}{2} \times 10^3$ |
|-----------|----------|---------------------------------------|---------------------------------------|---------------------------------------|---------------------------------------|
| (calc.) | (estim.) | (measured) | (BIJL) | (JOHNSON) | (calc. by BIJL) |
| 23 | — | — | — | | 17.4 |
| 11 | — | — | — | | 35 |
| 50 | m | 74 | 79 | 72 | 69 |
| 1.9 | — | — | — | | 104 |
| 3.3 | vw | — | 124 | | 121 |
| 78 | vs | 144 | 150 | 143 | 138 |
| 2.6 | — | — | — | | 155 |
| 8.5 | — | — | — | | 190 |
| 3.3 | w | 217 | 225 | | 225 |
| 3.3 | — | — | — | | 243 |
| 65 | s | 266 | 276 | | 278 |
| 2.7 | w | 255 | 294 | | 295 |
| 4.8 | — | — | — | | 328 |
| 20.8 | vw | — | 343 | | 347 |
| 2.2 | m | 356 | 365 | 348 | 382 |
| 4.0 | — | — | — | | 399 |
| 4.2 | vs | 411 | 417 | 404 | 416 |
| 2.8 | — | — | — | | 434 |
| 6.9 | vw | — | 466 | | 451 |
| 14.6 | — | — | — | | 486 |
| 4.8 | m | 496 | 508 | 491 | 502 |
| 4.4 | — | — | — | | 538 |
| 47 | s | 560 | 556 | | 555 |

BIJL and KOLKMEYER used the K -radiation of copper. Therefore on their films there are two series of lines, the ratio of the values of $\sin^2 \frac{\Theta}{2}$ of them for the same crystal face being 1:0.808. Half

of the lines observed by BIJL are ascribed to $K\alpha$ radiation, whereas the other part is ascribed to $K\beta$ radiation. In this laboratory the Röntgenradiation is usually filtered by a small nickel window, about 15μ thick. In this way the $K\beta$ radiation is completely absorbed, as follows from about a hundred Röntgen-patterns of other materials. With tin we found accurately the same lines as BIJL did, three excepted, the squares of sines being 0.124, 0.343 and 0.466 respectively ¹⁾.

It is very probable that only these three lines are to be considered as β lines, belonging to the very strong α lines 150, 417 and 556. In this case they should be 121, 338 and 450 respectively. JOHNSON also observed line 57. The latter is to be considered as the β line, belonging to the very strong line 72 (JOHNSON). From the small intensity of the β radiation it can be explained why the other β lines are missing. When all lines are to be considered as α reflections, then the agreement concerning the place of the lines, is certainly not sufficient for line 365. The nearest line is 382. The difference between the observed and calculated values of $\sin^2 \frac{\theta}{2}$ is 4%, which cannot be ascribed to errors of measurement.

As to the intensities, however, the disagreement is still more pronounced. According to the table of the calculated intensities, we would expect some exceedingly dark lines together with many weak ones; yet the intensities of the lines are not very unequal. Only at great angles of reflection some very strong lines appear. On closer examination of the table, we see, that the first two lines are missing, though they should have intensities, resp. 7 and 3 times stronger than the line 225 which is present.

Line 225 shows a second deviation. For the lines, which should lay on both sides, a double and equal intensity respectively is found theoretically. The question arises why are both lines missing? The same applies to the line 294 with the intensity 2.7. Why does line 398 fail? Line 343 should be very strong (intensity 20.8). BIJL estimates the intensity as very weak; on our foto's the line fails entirely. For the next line which is present, and even is estimated of medium intensity, the calculated intensity is about 10 times smaller than that of 338. Line 417, which is estimated as very strong, should have the same intensity as line 398 which is missing.

¹⁾ In the following we will call a reflection of which $\sin^2 \frac{\theta}{2} = 0.124$, reflection (line) 124.

We now compare the lines 343 and 417.

343, intensity calculated 20,8, estimated very weak

417, „ „ 4,2, „ „ strong.

According to the intensities we should expect the very strong lines 451 and 486 to occur on the foto's. It is very important that only one line is observed, i.e. 466, described by BIJL as to be very weak. This criticism could be continued, in my opinion however, the intensity of the lines sufficiently proves, that the structure, as given by BIJL, cannot be right. Against this structure still more objections can be made, a.o. that the proportion of the axes, as given by BIJL, is not simply related to that found by MILLER.¹⁾

When we summarise the objections to the interpretation of BIJL, we have:

1. for the absence of a number of lines no explanation is given.
2. the observed place of some lines is not in accordance with the calculated one.
3. the intensities do not satisfy.
4. the structure does not explain but very unsatisfactorily the proportions of the axes measured by MILLER.

By the following reasoning we come to a structure satisfying in all respects. As tin crystallizes in the tetragonal system the squares of sines are given by:

$$\sin^2 \frac{\Theta}{2} = A (h_1^2 + h_2^2) + B h_3^2.$$

Now the measured values satisfy this relation when we take:

$$A = 0.00875$$

$$B = 0.0588.$$

Hence the number of atoms per structure element is 8. When we take:

$$\text{specific weight} = 7,285$$

$$\text{atomic weight} = 118,7$$

$$N = 0,6062 \times 10^{24},$$

$$\text{wave-length } Cu_{K\alpha} = 1,539 \text{ \AA} \text{ (the average of } K_{\alpha_1} \text{ and } K_{\alpha_2})$$

we find by calculation:

$$A = 0,008745$$

$$B = 0,05878$$

when the value of the proportion of the axes given by MILLER (6,722) is accepted as being right.

The indices of the faces, which give lines of interference, as appears

¹⁾ Ann. d. Physik. u. Chem. 58, 660 (1843).

from the table, are all either even, having a sum divisible by 4, or all odd. In the case of regular crystals this condition is characteristic for diamond structure. Hence white tin has a tetragonal diamond-structure. No other lines than the calculated ones are present; on the other hand, all calculated lines are observed. Partly, however, they are doublets, laying so closely together that they cannot be observed separately. These double-lines can partly be recognized, because they are wider than the other ones; for those of them where the distance is greatest, distinct indications of double-structure can be seen on some of our films, a.o. for the lines 74 and 144. The observed intensities too are in accordance with the structure proposed here. The strongest lines on the film are marked with *S* in table II. Indeed, for these lines the calculated intensity is greatest, partly because the lines are close doublets.

The reflections of the faces 004 and 553 ($= 713$) are double. This is, because at big angles of reflection the K_{α_1} doublet is separated into its components. When we calculate from both the doublets the proportion of the wavelengths, K_{α_1} and K_{α_2} , we find resp.:

$$1.0027 \text{ and } 1.0025$$

whereas from the values given by SOMMERFELD¹⁾ follows:

$$1.00254.$$

As BIJL²⁾ pointed out, the grey tin possesses diamondstructure. Hence the structures of grey and white tin are very closely related.

In fig. 1 and 2 the structure-elements of grey and white tin are represented in natural proportion.

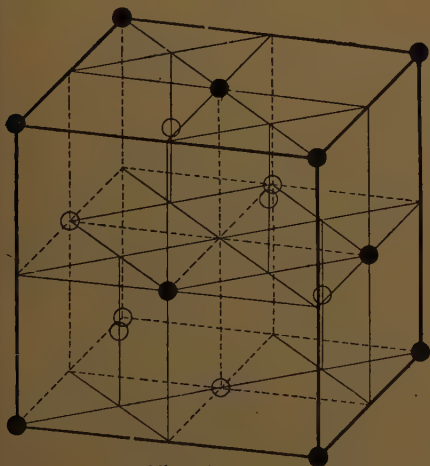


Fig. 1

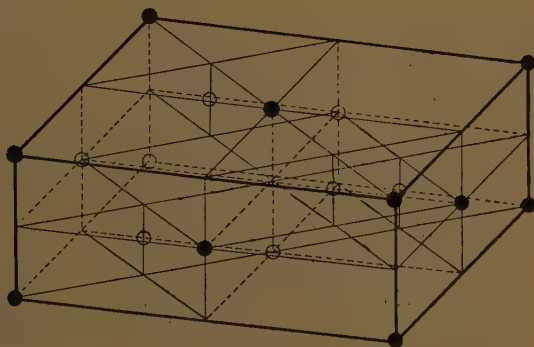


Fig. 2

¹⁾ Atombau und Spectrallinien 3e Auflage Braunschweig 1922, p. 188.

²⁾ l. c.

TABLE II.

| Distances | Intensity | | $10^3 \times \sin^2 \frac{\Theta}{2}$ | $10^3 \times \sin^2 \frac{\Theta}{2}$ | Indices |
|-----------------|-----------|---------|---------------------------------------|---------------------------------------|-------------|
| | (estim.) | (calc.) | (calc.) | (meas.) | |
| 4.54 | s | 22 | 70 76 | 74 | 220 111 |
| 6.40 | | 17 | 140 146 | 144 | 400 311 |
| 7.96 | | 4 | 216 | 217 | 331 |
| 8.98 | | 6 | 270 | 266 | 202 |
| 9.24 | s | 9 | 280 286 | 285 | 440 511 |
| 10.50 | s | 9 | 350 356 | 356 | 620 531 |
| 11.42 | s | 8 | 410 | 411 | 422 |
| 12.85 | s | 5 | 496 | 496 | 711 and 551 |
| 13.69 | | 4.3 | 547 550 | 548 | 113 602 |
| 13.87 | | 4.2 | 560 564 | 560 | 800 731 |
| 14.79 | | 1.3 | 617 | 615 | 313 |
| 15.11 | | 1.3 | 630 | 634 | 660 |
| 16.08 | s | 5.8 | 687 690 | 690 | 333 642 |
| 16.41 | s | 4.6 | 700 706 | 703 | 840 751 |
| 17.30 | | 2.1 | 757 | 755 | 513 |
| 17.71 | | 2.0 | 776 | 777 | 911 |
| 18.73 | s | 5.8 | 827 830 | 827 | 533 822 |
| 19.05 | | 1.9 | 846 | 840 | 931 |
| 20.97 | | 2.7 | 910 914 | 917 | 1020 771 |
| 21.64 and 21.82 | | 0.4 | 941 | 938 and 943 | 004 |
| 22.60 and 22.82 | | 2.5 | 967 | 963 and 969 | 713 and 553 |

In fig. 3 a section is given according to a (110) face through both the structure elements, which coincide here with the central points. The atoms of the grey tin are represented by small circles, those of the white tin by spots.

The transition of grey tin into white we can describe as follows.

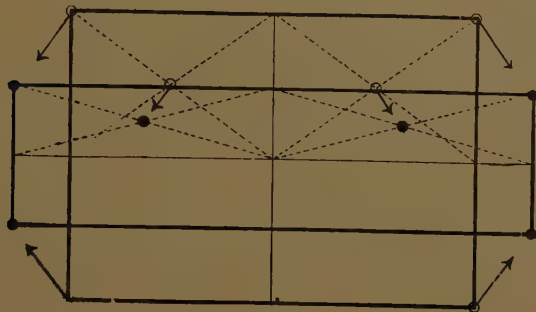


Fig. 3.

An elementary cube of grey tin, with a sidelength of 6.46 \AA , is pressed together in a direction perpendicular to the (100) face till somewhat more than half of the height. At the same time the atoms slide sideways, without changing their mutual position. In this way the structure-element of white tin is formed with the length of the sides 3.17 and 8.22 \AA . The smallest distance between two atoms changes with the transition from 2.23 \AA to 2.35 \AA . Notwithstanding the increase of specific weight with transition, the minimum distance between the atoms has increased.

Up to now tetragonal diamond-structure of elements has not yet been observed; some examples of compounds, however, are known. The structure which has most his resemblance with that of tin, is that of the copper-pyrites ($Fe Cu S_2$).

BURDICK and ELLIS¹⁾ describe this structure as follows: on each corner of the structure-element there is an iron atom, a second is in the middle of the basis-faces. Two Cu atoms are in the centre of the side-faces, whereas four sulphur-atoms are on the same place as the four inside tin-atoms in fig. 1. The proportion of the axes of this body is $1 : 1 : 0.985$.

The main difference between the two structures lays in the axial ratio, which in the case of copperpyrite only slightly deviates from 1, whereas with tin this ratio is 2.602 .

Practically at the same time as this paper was written there

¹⁾ C. L. BURDICK and J. H. ELLIS Journ. Am. Chem. Soc. XXXIX. 2518. (1917).

appeared a publication of Mr. POLANYI's, about the structure of white tin also. Mr. POLANYI proposes a new structure for white tin. The elementary cell contains 4 atoms, with the relative coördinates (000) $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ $(\frac{1}{2}0\frac{1}{2})$ $(0\frac{1}{2}\frac{3}{4})$.

The square of the axial ratio is $\frac{1}{2} \cdot 6.772$ instead of 6.772, as found here.

In truth there is no difference at all between the two structures, as Mr. POLANYI's structure-element is only the half of the element with 8 atoms, described above. The indices of table II are formed from Mr. POLANYI's notations by multiplying the first two by two.

From Mr. POLANYI's description the transition from white into grey tin seems somewhat complicated. Therefore I prefer the structure-element with 8 atoms.

Mr. KOLKMEYER kindly wrote me, that he made some new foto's with Copper K_{α} radiation only, and now also had found the same structure as given above.

Physical Laboratory of the "Philips" Glowlampworks.

Eindhoven, December 1923.

Anatomy. — “*Some vestibular-reflexes on the extremities from an anatomical point of view*”. By Prof. C. WINKLER.

(Communicated at the meeting of February 23, 1924).

There is a region in the human brain, of which the detailed description has been somewhat neglected and of which accurate drawings are seldom seen.

This region is the transition of the medulla oblongata into the basal part of the cerebellum.

It is well-known, that the restiform body — the pedunculus cerebelli inferior — is divided in two separate fields.

1^{ly} an oval area, a solid mass of fibres, going directly into the central cerebellar marrow.

2^{ly} a quadrangular area, with longitudinal fibre-bundles imbedded in and separated by reticular bands of grey matter, containing very large nerve-cells.

The latter field was called by MEYNERT the “*innere Abteilung des unteren Kleinhirnstiels*”; MONAKOW designs it with the letters I.A.K; others call it the corpus juxta-restiforme.

In it are seen two more or less distinct fibre-bundles; the one, the medial bundle, borders the lateral wall of the nucleus triangularis; the other, the lateral bundle, borders the medial side of the oval area.

Both receive their fibres from the larger cells of the nucleus triangularis. Both begin as very small bundles at the distal end of the triangular-nucleus, gradually they increase in extensity, as the nucleus sends new fibres to them. They are separated by grey reticulae belonging to the nucleus of DEITERS and reach their largest extensity at the proximal end of the triangular nucleus.

So they are seen in fig. 1 (f. med. and f. lat. I. A. K.), as their fibres are cut in an oblique direction, because they change their hitherto longitudinal path, and are bending to take a ventro-dorsal direction to enter the cerebellum.

In fig. 2 (at the right side), the lateral bundle has taken its ventro-dorsal direction, runs immediately under the ependyma of the aqueductus Sylvii, between ependyma and the origin of the brachium conjunctivum. The medial bundle (fig. 2 at the left side)

follows the same way. Both are tending towards the medial nuclei cerebelli.

The lateral bundle goes straight to the nucleus globosus. Most of its fibres end there. It is a tractus vestibulo-globosus (fig. 2 on the right side). But part of its fibres passes through this nucleus. Those are gathered in a well-defined field between nucleus globosus and nucleus emboliformis. These fibres bend medialward and reach the nucleus fastigii.

The medial bundle (fig. 2 on the left side, fig. 3 on both sides) passes through the nucleus globosus, fortifies the above-mentioned field (fig. 3 on the right side) or enters directly (fig. 3 on the left side) in the lateral wall of the nucleus fastigii. It is a tractus vestibulo-fastigii.

The nucleus fastigii however is provided with large multipolar nerve-cells spread between much smaller cells, which are the constituent elements of the nucleus globosus. The latter are the synapse-cells between the endarborisations of the two bundles and the large multipolar cells, whose axons leave the medial and ventral border of the nucleus fastigii and enter into the tractus uncinatus (RISSIEN RUSSELL), which crosses the midline, and covers directly the brachium conjunctivum at its dorso-lateral border (fig. 4).

This tract is well known by the famous experiment of VAN GEHUCHTEN, who found it degenerated on both sides, after a section in the midline between the two nuclei fastigii. It can be followed, with certainty, to the opposite nucleus DEITERS.

Each triangular nucleus is in this way connected with the homolateral and the contra-lateral nucleus of DEITERS.

Direct synapse-cells connect the triangular nucleus with the homolateral nucleus of DEITERS, which accompanies it laterally nearly from its beginning to its end.

The connection with the contralateral nucleus of DEITERS is more complicated. It is: nucleus triangularis, tracts to the cerebellar nuclei, nucleus fastigii, tractus uncinatus, nucleus DEITERS contralateralis.

From the nucleus of DEITERS originates the tractus DEITERO-spinalis bringing the nucleus in connection with the spinal motor-columns, and mostly with those belonging to the cervical and sacro-lumbar intermescentia.

A very simple scheme (fig. 5) shows those relations. The here described system must be a very old system. It is found in all mammalian. It gets myelinisation soon after that of the connection between triangular nucleus and the flocculus. Its myelinisation probably precedes that of the spino-cerebellar tracts.

In the foetus op 36 cM this system, with all its bundles entering or leaving the cerebellum, has got marrow long before the olivo-cerebellar or ponto-cerebellar pathes.

I believe that the connections of the triangular nucleus with both nuclei of DEITERS must act a part in the production of the reflexes, which the vestibular nerve causes in the extremities.

The following case, only reported in its main lines, may demonstrate it.

M., a farmer of 23 years, admitted in my clinic on the 18th of February 1923, was the oldest of six children, in a family not notorious for diseases.

Before November 1923 he never suffered. He first began to complain of headache above the eyes, soon afterwards localised in the occiput.

He however did his work until medio January. On 26th of January he took medical advice, complaining of dizziness and of uncertainty in walking.

He was brought in the hospital of Middelburg. Lumbar puncton was made (Pression of 17 cM. water, no cells, no globuline, WASSERMAN and SACHS-GEORGI's reaction—) and a slight optic neuritis was found. Thence he was sent to the clinic of Utrecht.

18. II. '23. He came there, a well-built man, 55,3 Φ . Temp. between 36°·6 and 37°·2 C., pulse between 92 and 108 p. m. No alterations in urine. No affection in thoracical or abdominal organs.

Lying in bed, he held his head bent against the chest. Backward movements of the head augment the pain in the occiput, they are done very slowly. Sideward movements of the head are well-done.

His gait is uncertain. He walks, bending his trunk backward, and with his eyes closed, he deviates to the right and to the left.

19. II. '23. No affection of the cranial nerves.

Dr. DE KLEYN (otologist) notes the following results:

Rhinoscopia anterior and posterior: No lesion.

Membrana tympani intact.

| Audition. | Lowest tone | C. | c ² (58) | g ⁴ (27) | RINNE. | SCHWABACH. | WEBER. |
|-----------|-------------|--------|---------------------|---------------------|--------|------------|------------------------|
| A. D. | normal | normal | 35 | 18 | — | shortened | localised to the right |
| A. S. | normal | normal | 58 | 18 | + | shortened | |

Vestibular reflexes. Seeing to the right: horizontal nystagmus to the right.

Seeing to the left: horizontal nystagmus to the left.

Seeing up and down: no nystagmus.

Barany-test. Spontaneous deviation of the right shoulder to the right in vertical direction; the vola manus turned up or down makes no difference.

No spontaneous deviation of the left shoulder in vertical direction.

There is no deviation in the horizontal plane, neither of the right, nor of the left shoulder.

the right, forced the left arm to deviate to the left during vertical movement *but never succeeded to bring the right arm to the left.*

3. An isolated motor paralysis of the left Vth nerve, with slight loss of sensibility in the tongue, and without any loss of sensibility in the cutaneous extension of the Vth nerve.

Seen from the view given in the scheme 5, those three symptoms were easily interpreted.

A circumscribed lesion, interrupting only the conductors from the left triangular nucleus to the right nucleus DEITERS was sufficient.

If placed at the proximal end of the *left* triangular nucleus in the I. A. K., this lesion would not damage the conducting paths of this nucleus to the left nucleus DEITERS. The influence of the left vestibular nerve upon the eyes and the left extremities existed as before. On the other hand no reactive stimulation could reach the right nucleus DEITERS. Thence there was no reaction of the right arm towards the left.

In the same line spontaneous deviation of the right arm to the right was interpreted. The prevailing of impulses of the right vestibular nerve on the right nucleus DEITERS, without impulses from the left side, was a necessity. Thence the spontaneous movement in vertical direction was forced to the right.

Finally the motor paralysis of the Vth nerve did not offer any difficulty. At that level the motor trigeminus-nucleus is immediately adjacent to the I. A. K. It was destroyed, and only slightly was damaged the sensory trigeminus-nucleus, whereas its spinal tract was without any injury.

The post-mortem, made by professor JOSSELYN DE JONGH, confirmed the here-defended views. A tuberculous tumour was found, exactly placed at the indicated spot in the I. A. K. (fig. 5, 6 and 7).

The tumour destroyed in the corpus juxta-restiforme the two before-mentioned bundles. It also destroyed the proximal end of the triangular nucleus and the whole of the motor trigeminus-nucleus. The proper sensory trigeminus-nucleus was partly injured, but the tumour did not reach far enough ventrally to injure also the exit of the spinal quintus-tract.

Distally the tumour ended far above the level of the origin of the VIth and VIIth nerves. Proximally the tumour did not injure the brachium conjunctivum but remained medial from it. The foto 6 is taken from a section through the greatest extension of the tumour.

The post-mortem however also brought out 9 other tuberculous tumours in the cerebellum. To give an impression of this complication

I have gathered them in a projection on the same level, somewhat distally from the place where the cardinal tumour was found.



Fig. 6.
Foto of the tumour.

From those tumours six were symmetrical. 1 and 2 were found at the proximal end of the lobus quadratus anterior; 3 and 4, in the central marrow of the cerebellum, proximal from the nuclei; 5 and 6 were found in the lobus semilunatus inferior, 8 in the lobus semilunatus superior, 7 in the anterior part of the midline (monticulus), 9 in the right brachium pontis.

It is well-known that BARANY poses the hypothesis that the cere-



Fig. 7.
Projection of all tumours on one level.

[illegible]

dent
embolus
glossus
pharynx
larynx
trachea

2.

4

4

for sp ce ve

br cony

to sp cony

to sp cony

to sp cony

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bellum organising impulses from the labyrinth and proprio-receptive impulses from the extremities, distributes them into special variations of the reflectory-tonus in the extremities. He suggests the existence of a centre for adduction-abduction and a centre for flexion-extension.

SVEN INGWAR, though not at all agreeing with the localisation of those centres, adopts the general idea of BARANY.

Their observations admit the possibility, that certain spots in the cortex cerebelli act in a different way upon the reflectory tonus of the extremities.

But they only may be related to a reflex-system on a high level (HUGHLINGS-JACKSON). Therefore loss or increase of reflectory-tonus is easily compensated. And as six of the tuberculous tumours are nearly symmetrical, and compensate each other influences, as the tumour in the midline is probably responsible for the uncertainty of the gait, only the tumours 8 and 9 may have acted on the reflectory-tonus of the right arm.

But it seems to me that the black tumour 10 has another meaning, and is responsible for the three here described cardinal symptoms.

The tumour interrupts a well known system of bundles, building together a reflex-system on a lower level, through which all mechanisms on the higher level are forced to pass.

The existence of this reflectory mechanism is necessary.

If the irritation of the vestibular nerve causes an increase of abduction-tonus in the homolateral arm, this function is reversed in an adduction-tonus in the contralateral arm.

It is difficult to understand that *one* Deitero-spinal tract superimposing the abduction-tonus on the vertical *homolateral* arm movements, will at the same time superimpose a reversed — an adduction-tonus — on the vertical movements in the *opposite* arm.

Therefore the existence of another reflectory-mechanism is necessary. This is found in the complicate system in the corpus juxta-restiforme.

DESCRIPTION OF PLATE.

Drawings of sections through the cerebellar nuclei.

Fig. 1. Section at a level, where the oval area of the restiform body deviates in the marrow of the cerebellum.

Fig. 2. Section through the brachia pontis. Nucleus globosus, nucleus emboliformis and the frontal end of the nucleus dentatus are seen.

Fig. 3. Section through the origin of the brachium conjunctivum. All four nuclei are sectioned.

Fig. 4. Section through the tractus uncinatus. Only the nucleus fastigii is seen.

Aq. = Aquaeductus Sylvii; *br. conj.* = brachium conjunctivum; *br. pont.* = brachium pontis; *c. r.*, *c. r. I.*, *c. r. II* = corpus restiforme; *c. trap.* = corpus traperoides; *f. lat. and f. med. I. A. K* = fibrae laterules et fibrae mediales corporis juxta-restiformis; *fibr. tegm. cereb.* = fibrae tegmento-cerebellares; *fibr. t. c. med.* = field of the medial bundle of fibrae tegmento-cerebellares; *G. VII* = genu nervi facialis; *lemn. med.* = lemniscus medialis; *n. dent.*, *n. embol.*, *n. glob.*, *n. fast.* = nuclei dentatus, emboliformis, globosus, fastigii; *n. mot. and n. sens.* *N. V.* = motor en sensory nucleus of the nervus trigeminus; *n. tegm.* = nucleus tegmenti; *n. triang.* = nucleus triangularis; *n. ventr. N. VIII.* = ventral nucleus of the nervus octavus; *n. VI.* = nucleus nervi abducentis; *N. VIII.* = nervus octavus; *ol. sup.* = oliva superior; *ped. flacc.* = pendunculus flacculi; *r. VII* = radix nervi abducentis et facialis; *str. med.* = stria medullaris ventriculi quarti; *tr. ol. ce.* = tractus olivo cerebellaris; *tr. sp. ce. do.*, *tr. sp. ce. ve.* = dorsal and ventral spino cerebellar tracts; *tr. sp. N. V.* = tractus spinalis nervi trigemini; *tr. unc.* = tractus uncinatus.

Physics. — *“Light emitted from solid Nitrogen when bombarded with Cathode Rays, and its bearing on the Auroral Spectrum”.*

By Prof. L. VEGARD (Christiania). (Communicated by Prof. H. KAMERLINGH ONNES). (Communication N°. 168d from the Physical Laboratory at Leiden).

(Communicated at the meeting of February 23, 1924).

Investigations recently carried out on the auroral spectrum led me to the view that the upper strata of the atmosphere above 90 km. say, were mainly composed of Nitrogen frozen into minute dust particles. These particles were supposed to be more or less electrically charged through the photoelectric effect of the sun rays and in this way the effect of gravity was counterbalanced. With regard to details I must refer to my papers¹⁾.

As a consequence of this hypothesis the auroral spectrum (at any rate all stronger lines) should originate from Nitrogen and should be a type of spectrum produced when solid Nitrogen dust — perhaps mixed with some gas — was bombarded with electric rays. Above all, the predominant green line ($\lambda = 5577$) should be a line peculiar to the solid state of Nitrogen.

Even if our hypothesis be right it is very difficult to reproduce exactly the conditions under which light is emitted in the higher strata of the atmosphere. First of all we do not know exactly the temperature and the properties of the rays producing the aurora, but apart from this there is the difficulty of producing a cloud of Nitrogen dust.

As already mentioned in my previous paper we might, however, at any rate approximately, reproduce the conditions under which the auroral light is formed, by producing solid Nitrogen e.g. by means of liquid hydrogen, and bombard it with electric rays of some sort.

My laboratory at Christiania had not the necessary equipments for experiments of this kind, but fortunately through the generosity of Professor KAMERLINGH ONNES I was able to take up the experiments at the laboratory of Leiden.

¹⁾ C. R. t. 176, p. 947 and p. 1488, 1923., Phil. Mag. Vol. XLVI p. 193 and p. 577, 1923. Zeitschr. f. Physik B. 16, p. 367, 1923. Kristiania Vid. selsk. skr. Mat. nat. Kl. Nr 8, 9, 10, 1923.

My first object was to examine the possible light effect produced when solid Nitrogen was bombarded by *cathode rays*.

Thanks to the help and advice I got from Professor KAMERLINGH ONNES and Professor W. H. KEESOM, and thanks to the unique equipment and organisation of the laboratory for this kind of work, and last but not least thanks to the marvellous skill of the trained staff of the laboratory, I was able to carry out these experiments in the course of about four weeks. I obtained the very light effect which I had sought for, and I was able to make a first study of it. The effect found brings forward a number of questions, and I intend to continue the work at the laboratory of Leiden.

Presently I am going to give a short description of this first and fundamental experiment and the results obtained.

Experimental arrangements.

A general plan of the experimental arrangement is given in fig. 1. It consists principally of the two parts: The cooling apparatus I. and the vacuum tube II. for the production of cathode rays.

A separate drawing of the cooling apparatus is given in fig. 2. It consists of an inner metallic receiver for the liquid Hydrogen A. At the bottom of this receiver is fixed a copper rod ending in the free surface *c*, cut at an angle of 45° , just like the anticathode of an X-ray tube. At the upper end the receiver is soldered on to a long brass tube *D*, *D*, which carries the long double walled vacuum tube *a*, *a*, for the introduction of liquid Hydrogen and the side tube *g* for the outflow of the evaporated Hydrogen. The quantity of Hydrogen contained in the receiver is indicated by the floater *d*, attached to the spiral in the glass tube *b*. The receiver and part of the copper rod and the brass tube is soldered on to a wider glass tube *E*. The space between the metallic receiver and the glass tube can be evacuated through the side tube *f*.

To prevent cracking through changes of temperature the metallic part is connected with the upper end of the glass tube by a metallic spring arrangement, which is kept under a certain constant tension by the metallic spirals *e*, *e*.

The cooling apparatus is fixed to the discharge tube by means of a ground glass joint as indicated in fig. 1.

The discharge tube consists of two glass tubes (4) and (11) fig. 1, connected by means of the metallic cylinder (9). The cathode rays are formed by the Wehnelt cathode (10) and are made to pass along and narrow boring through the metallic cylinder (anode) and

into the observation room (4) where the rays strike the end surface (6) of the copper rod coming from the Hydrogen receiver.

The inside of the tube (4) is silvered and put in metallic connection with the anode, and only a vertical slit about 1 cm. of breadth in front of the copper surface is transparent.

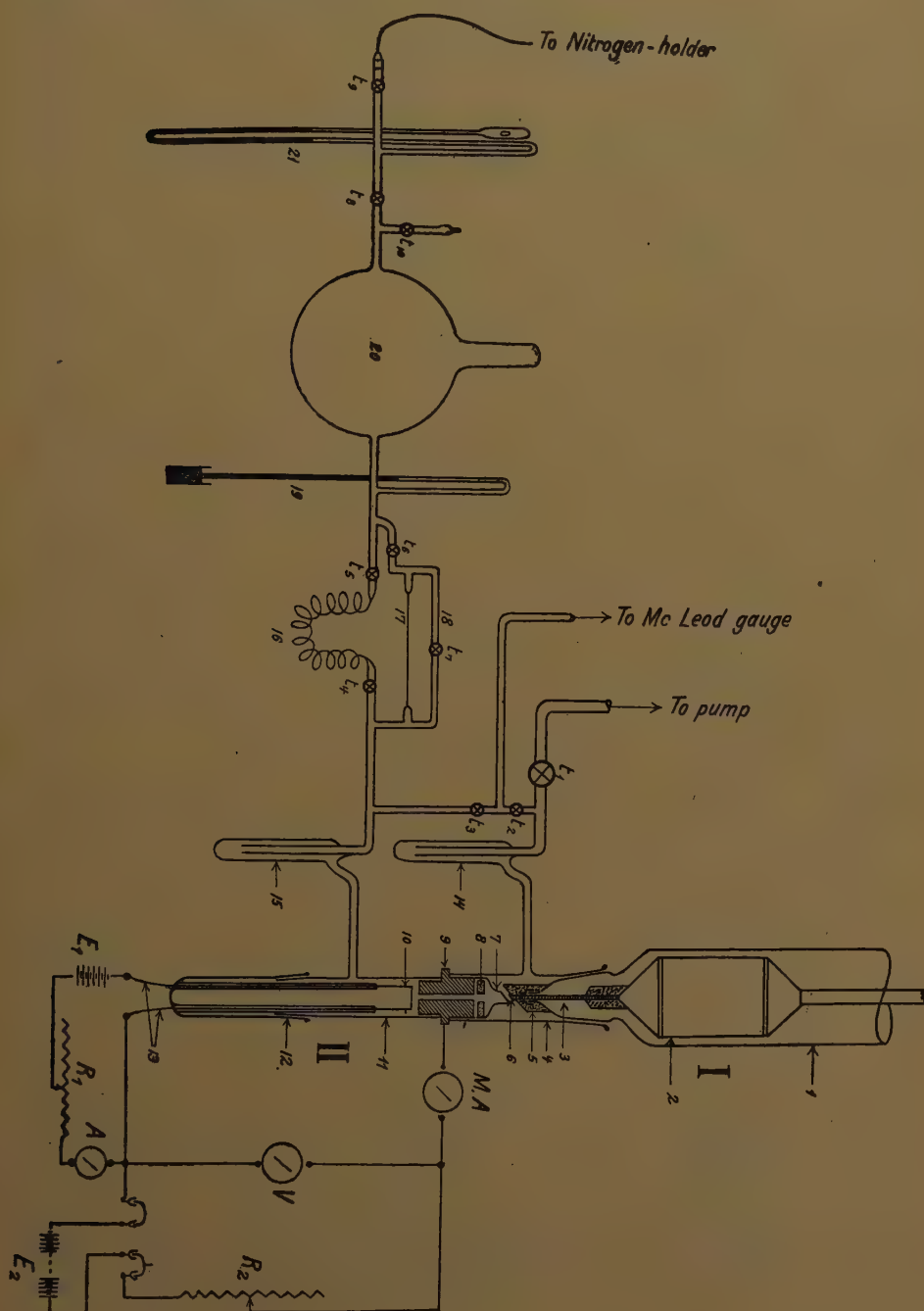


Fig. 1.

During the experiment Nitrogen gas contained in the large bulb (20) is continually streaming into the discharge room through a narrow capillary tube (16) which can be closed at both ends by the taps t_1 and t_2 . The observation chamber is connected with a high vacuum pump. The traps (14) and (15) cooled by liquid air prevent any kind of vapours from entering discharge- and observation room.

In this way a high vacuum can be maintained in the observation room surrounding the copper surface, which is going to be cooled by liquid hydrogen, while at the same time the pressure in the discharge room is sufficiently large for the good working of the Wehnelt cathode. The pressure on both sides of the anode could be measured by a Mc. LEOD gauge. The bottom part of the copper rod is surrounded by a small glass cup (5) filled with isolating material, and only the very bottom surface of the copper rod is free.

In order to improve the heat isolation round the cold surface still more a silvered quartz plate (8) with a hole in the middle is placed on the top of the anode, and this quartz plate is surrounded by a glass cup ending in a tube (7) just in front of the copper surface.

The electrical arrangement is seen from fig. 1. The heating current was measured by means of the ammeter A , the discharge current with the milliamperemeter (MA) and the effective potential determining the velocity of the cathode rays was measured with the voltmeter (V).

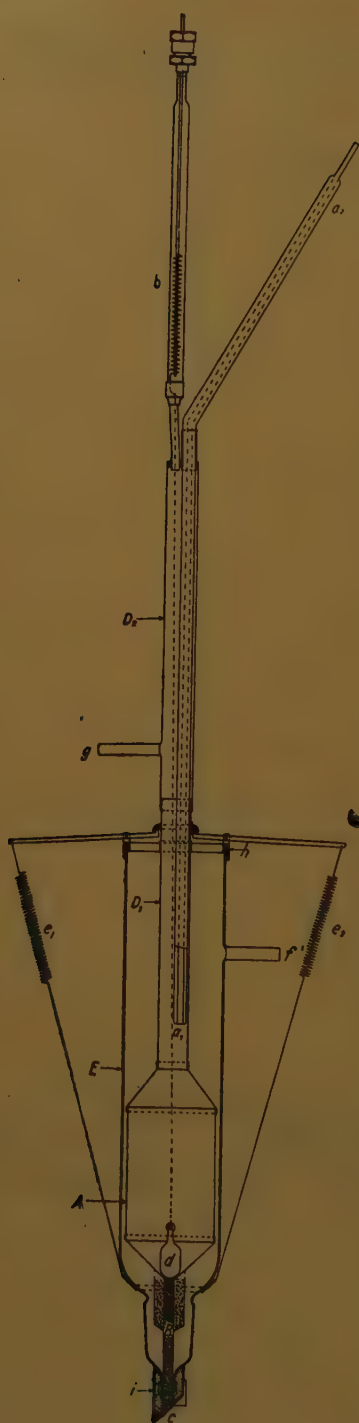


Fig. 2.

Procedure.

When the liquid Hydrogen was introduced into the cooling apparatus and the copper surface was made cold, a comparatively heavy current of Nitrogen was made to pass into the discharge tube by opening the tap t_6 , or both t_6 and t_7 simultaneously. The gas is made to pass close up to the cold surface, where part of it is frozen and the rest is escaping through the pump. When a fairly thick layer (it appeared to be about 0.5—1 mm.) of solid Nitrogen is formed, the current of nitrogen is reduced, partly by closing the taps t_6 and t_7 and partly by reducing the pressure in the bulb (20) and the rays can be put on.

Observations.

After the arrangement for producing the cathode rays had been tested and the suitable regulation for the gas stream was found, the cooling apparatus was put up and the first experiment could be carried out on the 16th of January this year.

A layer of solid Nitrogen on the copper surface was easily formed under the experimental conditions described. At first cathode rays with a tension of about 75 volts were put on, and the solid Nitrogen layer was seen to give out a faint luminosity, which in a spectroscope showed the blue and violet negative bands. The tension was increased to 200 volts and a line in green (near the blue part) was seen. The wavelength of this line was later found to be about 5230 Å. The luminosity was still faint and not very conspicuous.

Unfortunately the hydrogen receiver was not perfectly tight and in consequence the vacuum of the cooling apparatus was imperfect, and the hydrogen evaporated in the course of 10—15 minutes.

By pouring on new liquid Hydrogen the solid Nitrogen layer was kept for a time so long that a spectrogram could be taken with about half an hours exposure. The potential was about 200 volts and the current through the tube 1,5 milliamperes.

The spectrograph used for this investigation was a small one which I brought with me from Christiania. In fact it is one of the spectrographs which I used last year for the investigation on the auroral spectrum. It has a rather small dispersion, but was chosen for this first experiment on account of its high light power. A neon lamp was used for the comparison spectrum.

A reproduction of this first spectrogram from solid Nitrogen is given on the top of the plate I (A:1).

Already this result was very promising, for I could see at a glance on the photographic plate that the spectrum bore a striking resemblance to the auroral spectrum. The negative Nitrogen bands were concentrated into a few fairly sharp lines just as in the auroral spectrum, and, besides, the green line already mentioned near the blue part as well as a diffuse band appeared, which had its maximum intensity at a wave length corresponding to that of the green auroral line. (5577).

The leak of the cooling apparatus had increased and it had to be taken down, but already on the morning of the 19th of January the experiments could be continued with an apparatus which was now in perfect working order, and by refilling it every now and then with liquid Hydrogen I was able to work on the same layer of solid Nitrogen for about five hours. It was my plan now to increase the velocity of the rays, and in consequence the effective potential was raised to about 500 volts. The effect was almost perplexing. The layer of solid Nitrogen when bombarded with cathode rays was made brilliantly luminous and showed the same green colour which is so characteristic for most aurorae.

In the spectroscope I now could see two strong green lines, the one already mentioned near the blue part, and which we shall denote by N_2 , and another very near the yellow part which we shall call N_1 . The latter seemed to consist of several lines, the intensities of which changed according to the conditions of the experiment.

A spectrogram was taken (A. 2 on the plate) with 15 minutes exposure and a potential of about 500 volts. In blue and violet the spectrum obtained was now the same as before, and the green line N_2 is also present, but besides there appears on the plate the narrow band or group of lines N_1 , which has sprung out near the yellow part.

The dispersion is not sufficiently large to separate the individual lines in this band. But on the plate as well as in the spectroscope there seem to be two fairly strong lines, and the measurements of the plate show that the one on the side towards blue, as far as can be judged from the present spectrograms, has the position of the green auroral line.

The relative intensity of N_1 as compared with N_2 , or as compared with the blue part of the spectrum changes enormously with the velocity of the rays.

When the potential was lowered to about 350 volts the band N_1 disappeared, and in the spectroscope only the line N_2 was

seen. A. 3 is a spectrogram taken under this condition. The line N_1 is no longer to be seen on the plate.

If, however, we increase the potential, the intensity of N_1 increases with great rapidity. With a tension of about 700—750 volts it became most predominating, and the solid Nitrogen layer was now shining with great brilliance.

When the cathode rays were playing on the solid Nitrogen surface moving round about, the similarity of this phenomenon and an auroral display was indeed striking.

With this high tension of about 700—750 volts I took two spectrograms (A. 4 and A. 5). Although the time of exposure was only 5 minutes N_1 is considerably overexposed, while the other lines are fairly weak. N_1 is now predominating over all other lines, just as the auroral line is predominant in the auroral spectrum. All spectrograms were taken on orthochromatic "Flavin"-plates.

As soon as I had obtained the strong green light, a most remarkable effect was observed. When the discharge was broken and the cathode rays cut off, *the layer of solid Nitrogen remained luminous and showed the same green colour as during the bombardment of the rays.*

The solid Nitrogen layer had exactly the appearance of a phosphorescent body, and although we are dealing with a luminosity emitted from an elementary substance, the light, at any rate the green part of it, may probably best be regarded as a type of phosphorescence. The intensity of the *after glow* diminished very slowly. I took an observation and found that *even 5 minutes after the cathode rays were cut off the layer of solid Nitrogen was still distinctly seen to emit green light.*

The line N_2 was also observed with a spectroscope from HILGER

TABLE I.

| λ . | | Reading. |
|-------------|--------|----------|
| 1 Ne. | 5852.5 | 55.521 |
| 2 " | 5748.2 | 55.840 |
| 3 " | 5400.5 | 57.370 |
| 4 " | 5300.7 | 57.648 |
| 5 He. | 5015.7 | 59.443 |
| N_2 | | 58.180 |

provided with a micrometer screw, the Neon and Helium spectra being used for comparison.

The readings for N_2 and some known lines are given in the table I.

It was also my intention to take similar readings for the broad N_1 line, but when I was going to take the observations, the cooling apparatus got a leak, so the Hydrogen soon evaporated.

In order to get a more accurate determination of the spectrum emitted from solid Nitrogen I should want a spectrograph of a larger dispersion, and as I had already succeeded in taking a number of spectrograms with the small spectrograph, I decided to stop further observations for some time in order to make preparations for more accurate measurements.

The present paper is therefore merely to be considered as a preliminary communication which only intends to give a first announcement of the effect and its important bearing on the auroral problem.

Wavelength and Intensity of N_1 and N_2 .

After my arrival at Christiania at the end of January the plates were measured in the ordinary way with a microscope mounted to a long micrometer screw and registrams of the spectra were taken with a Moll-microphotometer from the firm Kipp & Zonen.

As already mentioned the dispersion is very small, and the wavelength cannot be very accurately determined. The lines in the blue part are so characteristic that they need not be measured in order to be identified. I have therefore merely measured the green lines N_1 and N_2 on the spectrograms A. 2, 3, 4, 5.

As already mentioned N_1 is not a single line, but the dispersion of the apparatus is not sufficiently large for their separation. Spectrogram (2) gives distinctly the impression of two lines with the weakest towards the yellow. The strongest of these — as far as can be judged from the present spectrograms — has the position of the auroral line.

I have therefore found it the best only to give limits of the group N_1 . But we shall have to remember that the band is broadened by overexposure and through the breadth of the lines on the plate. We consequently get a much too large wavelength interval for the group N_1 . The results are given in table II.

The spectroscopic observations of the line N_2 gave the following results:

Using the lines (1, 4, 5) table I, we obtained for N_2 : $\lambda = 5233,8$,

while the lines (2, 3, 5) gave $\lambda = 5239.7$. The mean of these two gives $\lambda = 5237$. The spectroscopic observations give as we see a some-

TABLE II.

| Spectrogram. | N_1 . | N_2 . |
|--------------|---|---------|
| 2 | $\left. \begin{array}{l} 5537 \\ 5653 \end{array} \right\}$ | 5220 |
| 3 | Not present | 5219 |
| 4 | $\left. \begin{array}{l} 5519 \\ 5689 \end{array} \right\}$ | 5230 |
| 5 | $\left. \begin{array}{l} 5522 \\ 5686 \end{array} \right\}$ | 5226 |
| | Mean | 5224 |

what larger value than the spectrograms. The mean of the spectrographic and the spectroscopic values gives for N_2 the wavelength **5230**.

Registrams of the five spectra from solid Nitrogen are given in fig. 3. The wavelengths of the corresponding auroral lines are given at the head of the plate, and their position is marked with an arrow. The approximate value of the potential corresponding to each registram is given on the plate. The great variability of N_1 and N_2 is clearly seen. A more accurate determination of the way in which the intensity of N_1 and N_2 varies with the velocity of the cathode rays must be left for further investigations. The present experiments indicate that the line N_2 is excited at a tension somewhat under 200 volts and that its intensity relative to that of the negative bands first increases to a maximum at about 400 volts, after which it again diminishes. The group N_1 is excited at a potential of about 400 volts and its intensity increases very rapidly, but also there we shall probably have a velocity for which the relative intensity of N_1 is a maximum.

Comparison with the Auroral spectrum.

It appears that the bombardment of solid Nitrogen with cathode rays has given just the light effect which I had sought for. When the velocity of the rays is raised above a certain limit, the solid Nitrogen is brought to emit a green light concentrated into a few lines consisting of the group N_1 and the line N_2 . For small velocities N_2 is dominating, but when the velocity increases N_1 takes the lead. Now the strong auroral line is lying in the group N_1 and as far as can be judged identical with one of the strongest components, and I think there can be no doubt that in the group N_1

we have obtained the light effect which explains the origin of the green auroral line.

The fact that N_1 consists of several lines close together while in most aurorae only one line is possible is no serious objection, for we must remember that the relative intensity of the green lines is found to change enormously with fairly small variations of the experimental conditions. Now the auroral light, also no doubt emitted from solid Nitrogen, is emitted under conditions which may differ considerably from those of my experiments. First of all the light is emitted from fine particles of submicroscopic order of magnitude. Secondly the temperature, the velocities of the rays and even the type of rays may be different.

Now it is also possible that all lines in the group N_1 are present in the aurorae but with another intensity distribution. The well known northlight-investigator CARLHEIM GYLLENSKIÖLD has occasionally during intense auroral displays observed lines lying near to the auroral line.

Also the line N_2 , which at the first sight came somewhat unexpected to me, is found by further examination to have a position corresponding to a quite conspicuous line which can be observed in somewhat strong auroral displays. Although the earlier observations are not very accurate a large number of observers give a line at the same part of the spectrum. Taking the mean of 10 observations which are to be referred to the same line, I found for the wavelength ¹⁾ 5230, which is just the wavelength found for the line N_2 emitted from solid Nitrogen. Considering the errors of the determination, the almost perfect agreement is more or less accidental. The fact, however, that both N_2 and N_1 correspond to the two most conspicuous lines in the green part of the auroral spectrum cannot be accidental, and we conclude that the conspicuous green auroral spectrum is due to the peculiar light effect produced in solid Nitrogen.

This conclusion is also confirmed in a most striking way by comparing the other part of the spectrum from solid Nitrogen with the auroral spectrum. In the series B of the plate are reproduced some photographs of auroral spectra, and the second spectrum from solid Nitrogen is given underneath. Spectrum B. 1, is a reproduction of an auroral spectrum obtained this winter with a large quartz spectrograph. Spectrum 2 is an enlarged copy of an auroral spectrum taken with the same small spectrograph as the one used in Leiden, with the difference that by the auroral spectrum a cylindrical lens was used in front of the plate in order to increase the light power.

¹⁾ See H. KAYSER, Handbuch d. Spektr. V. 5. p. 56—57.

These two spectrograms (1) and (2) were taken on Imperial eclipse plates, which are not sensitive to green. B. 3, on the plate is an enlarged reproduction of an auroral spectrum taken with the same small spectrograph, but on a panchromatic plate.

Comparing the spectrum of solid Nitrogen with the known Nitrogen spectrum of the aurorae, we see that in both cases the spectra are dominated by the negative band heads 4708, 4278, 3914, and also in the case of solid Nitrogen we get the same reduction in the number of lines and bands which is so peculiar to the auroral spectrum. Both in the auroral spectrum and in the spectrum of solid Nitrogen the three strongest bands are followed by a second head with a somewhat smaller wavelength than the principal heads, and the relative intensities seem to be the same in both cases. Besides these three principal heads and their "secondaries" four other lines, two on each side of 3914 are distinctly seen in the violet and ultraviolet part of the spectrum, and these lines (wavelength 4058, 3998, 3805, 3756) appear in the auroral spectrum with the same relative intensities. Two other faint lines ($\lambda = 4344$ and $\lambda = 3943$) are also to be seen both in the auroral spectrum and in that of solid Nitrogen. Although the strongest heads are much overexposed, the lines mentioned are the only ones appearing in the blue and violet part of the spectrum from solid Nitrogen, and all of these appear in the auroral spectrum and with the same typical relative intensities.

The close agreement between the auroral spectrum and that from solid Nitrogen is also clearly seen by comparing the registrants in fig. 3 with the registrants in fig. 4, representing the auroral spectrum which we have reproduced on plate B. 1, and which is taken with a quartz spectrograph.

The striking similarity between the known Nitrogen spectrum of the aurorae and the spectrum produced in solid Nitrogen is even better seen directly from the plates than it can be described by words, and as the result of the comparison we may say: *The spectrum shown by the aurorae is exactly of the same type as that produced when solid Nitrogen is bombarded with cathode rays.*

In addition to the conclusive evidence furnished by the spectra we have also the characteristic after-glow shown by the solid Nitrogen.

When in the winter 1912—13 I had — for the first time — the opportunity of taking auroral observations near the auroral zone, I was soon struck by the phenomenon ¹⁾ that after violent displays of

¹⁾ L. VEGARD, Berichte über eine Expedition nach Finmarken 1912—13 Kristiania Vid. Selsk. Skr. Mat. Nat. Kl. N^o. 13, p. 48.

auroral rays and draperies, the sky was left behind with a diffuse green after-glow which was gradually fading away and could be observed for about 5—10 minutes after the actual precipitation of electric radiation had stopped.

This phenomenon is now shown to be a simple consequence of the fact that the green auroral light originates from solid Nitrogen particles. The rapidity with which the cosmic after-glow fades away

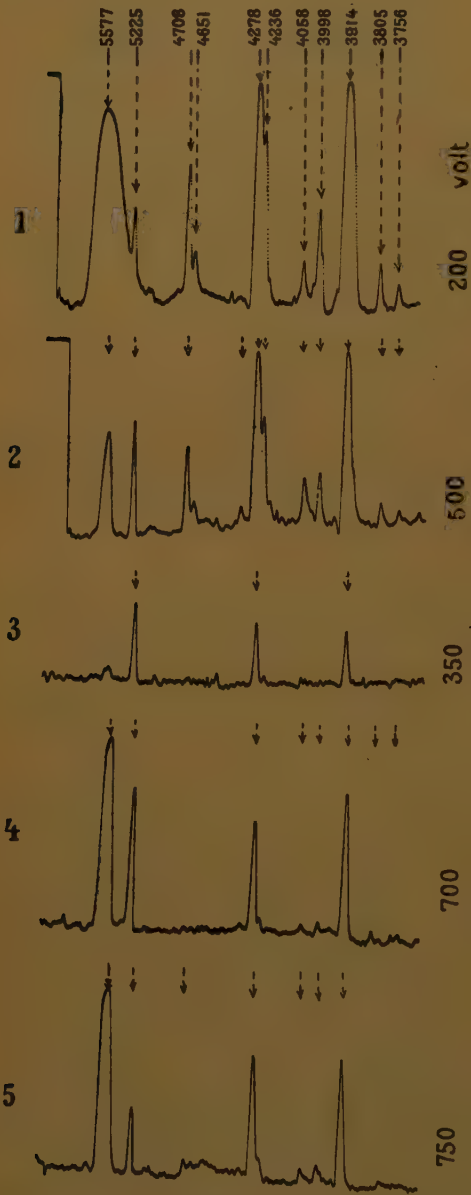


Fig. 3.

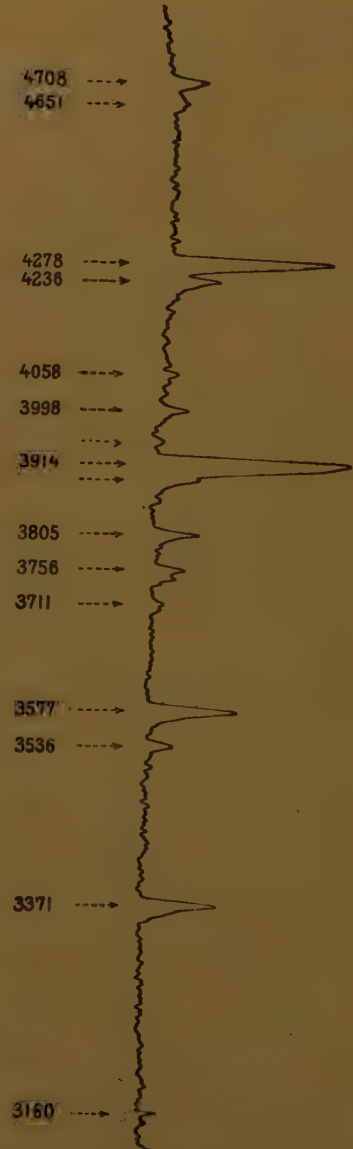


Fig. 4.

is also seen to be about the same as that observed in the case of solid Nitrogen.

The great variability in the intensity of the green light given out by solid Nitrogen will certainly account for many of the colour variations shown by the aurorae. According to the velocity of the cosmic rays the colour may change from violet, bluish white to intense yellow-green. As already mentioned in my first paper the intense red colour should be due to Nitrogen in the gaseous state¹⁾.

As a result of the whole comparison we can say that our experiments have shown *that the typical auroral spectrum is emitted from Nitrogen in the solid state, and the hypothesis which I have previously put forward with regard to the state of the upper strata of the atmosphere has been confirmed.*

As mentioned in my previous papers the view that the upper strata of the atmosphere consist of solid Nitrogen particles has far reaching consequences and enables us to see a number of cosmic phenomena in a new light.

It will make it necessary to take into account the scattering effect of these particles for the theory of the blue sky. We are led to a simple explanation of the zodiacal light, the twinkling of the stars, the colour variation of the aurorae, the reflection in the upper strata of the atmosphere of electric and acoustic waves. If also other gases than Nitrogen, when in the solid state, can be brought to emit line spectra, when exposed to radiations, new possibilities are given for understanding the state of the stellar nebulae and the origin of the nebular lines²⁾. With regard to details I must refer to the previous publications³⁾.

The fact that we are able to reproduce the typical auroral spectrum in laboratory experiments is no less important for the further study of the aurorae themselves. By bombarding solid Nitrogen with electric rays and making an accurate comparison with the auroral spectrum we may be able to tell with certainty what kinds of electric rays may be engaged in producing the auroral displays in the various cases. We may further be able to tell a good deal about the velocity of the cosmic rays and finally we may get a fairly definite knowledge with regard to the temperature of the dust particles in the auroral region.

But apart from its important bearing on cosmic problems, the light effect produced in solid Nitrogen is in itself of great interest

¹⁾ See e.g. Phil. Mag. 46. p. 595, 1923.

²⁾ See: Kristiania. Vid. Selsk. Skr. Mat. nat. Kl. N^o. 10, p. 16, 1923.

³⁾ loc. cit.

from a purely physical point of view. It shows that an elementary solid substance at low temperatures, when bombarded with cathode rays, may be brought to emit a kind of line spectrum, which at any rate partly is typical for the solid state, and is not obtained when the substance exists in the gaseous state composed of free molecules.

No less interesting is the fact that a band-spectrum which is emitted in the gaseous state is also given out by the substance in the solid state.

These facts might give us some valuable clue for the explanation of the negative band spectrum, and at the same time give us some information with regard to the way in which the atoms are bound up in the molecules and in the crystal grating.

It will be evident from what is said, that the effect raises a number of important questions and calls for further investigations in various directions, and I hope to be able to push things a little further by continuing the investigations at the Cryogenic Laboratory of Leiden.

In conclusion it is a duty and a great pleasure to me to express my heartiest thanks to Professor KAMERLINGH ONNES for giving me the privilege of carrying out these experiments at his Cryogenic Laboratory at Leiden, for his invaluable help and advice and for the interest he has taken in my work, I also wish to express my heartiest thanks to Professor KEESOM for the indefatigable help given to me, and for the kind interest shown throughout the whole work. It is needless to say that the success of the work has only been possible through the unique equipment and organisation of the Leiden Laboratory.

EXPLANATION TO THE PLATE.

SERIES A.

| | | | | | |
|----|---------------------------|---------|------------|----------|---------|
| 1. | Spectogr. solid Nitrogen. | Tention | 200 volts. | Exposure | 30 min. |
| 2. | " | " | 500 | " | 15 " |
| 3. | " | " | 350 | " | 10 " |
| 4. | " | " | 700 | " | 5 " |
| 5. | " | " | 750 | " | 5 " |

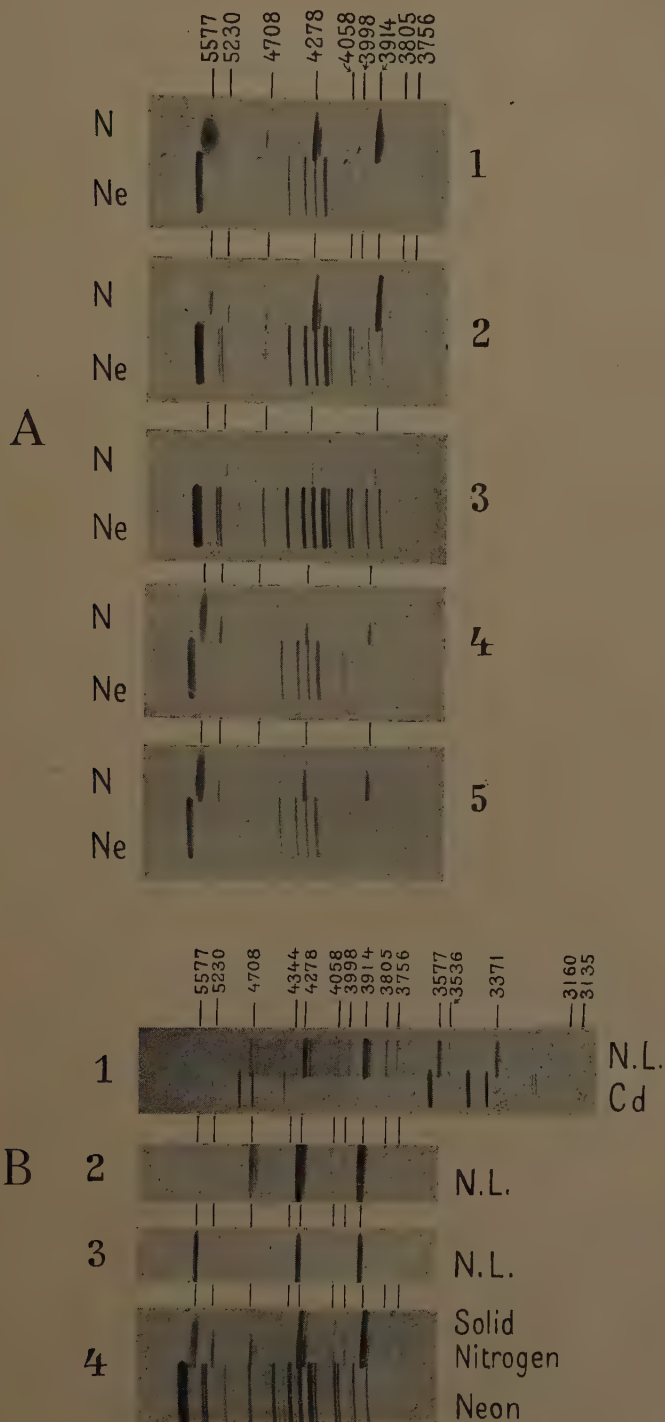
Neon spectrum for Comparison.

SERIES B.

| | | | |
|----|-------------------------------------|----------------------|--------------------------|
| 1. | Northlight spectr., | Quartz spectrograph, | Imperial Eclipse plates. |
| 2. | " | Glass | " |
| 3. | " | " | Panchromatic |
| 4. | Spectrum from solid Nitrogen (A 2). | | |

Wavelength and position of Auroral lines given at the head of each series.

L. VEGARD: "Light emitted from solid Nitrogen when bombarded with Cathode Rays, and its bearing on the Auroral Spectrum".



Mathematics. — “*A Representation of the Line Elements of a Plane on the Points of Space*”. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 29, 1924).

1. In the first chapter of his thesis for the doctorate ¹⁾ Dr. G. SCHAAKE has communicated a method to represent the line elements of a plane φ by the points of space. In order to reach this aim by another way I assume a straight line b in φ , a straight line a and a point M outside φ . The point P of the line element $e(P, l)$ defines the straight line $m = PM$, the line l the point $B = lb$. If α is the plane through B and a , I consider the point $S = m\alpha$ as the image of e . Inversely a point S generally defines an element e . For SM cuts φ in P , $\alpha = Sa$ cuts b in B , and $l = PB$.

2. There are three systems of *singular line elements*. For $e = (B, b)$ the point of intersection lb is indefinite, so that also the plane α becomes indefinite; hence any point of the ray BM may be considered as the image S . The *singular elements* (B, b) form a system $(0,1)$, their images are the ranges of points (S) on the rays of the plane pencil (M, β) where $\beta = Mb$.

Let μ be the plane through M and a , c the straight line $\mu\varphi$, some point of c , $A_0 = ac$, $D = bc$. For the element $e = (C, c)$ $m = CM$ lies in the plane $\alpha = \mu$, so that any point of m may be considered as image S . Also the *singular elements* (C, c) form a $(0,1)$; their images are the point ranges (S) on the rays of the plane pencil (M, μ) .

For the element $e = (D, l)$ we have $B = D$, $\alpha = Da = \mu$, $m = DM$; any point of the straight line $d = DM$ may therefore be considered as an image. The *singular elements* (D, l) form a system $(1,0)$.

For the inverse representation M is a *cardinal point*, for each point of φ may be considered as a point P . As $\alpha = \mu$, $B = D$, l always passes through D ; M is therefore the image of each element of a null system $N(1,0)$.

Every point A of a is *singular*, for if $S = A$, α is indefinite and

¹⁾ Afbeeldingen van figuren op de punten eener lineaire ruimte. P. Noordhoff, Groningen, 1922.

$P = (AM, \varphi)$; hence A is the image of each element (C, l) . Accordingly the line elements of an $N(0,1)$ correspond to the singular points A ; only the points of c are null points.

Also the points $S = B$ are *singular*, for in this case l is indefinite, hence B is the image of each element (B, l) .

The image S of any line element of which $l = PA_0$, coincides with the point P . The point A_0 is the image of all the elements (A_0, l) , hence a *singular* point S .

3. The straight lines l of a system $(1,0)$ form a plane pencil round a point P_1 . The image of this $(1,0)$ is the point range (S) on PM .

The points P of a $(0,1)$ lie on a line l_1 . The image of $(0,1)$ is the point range (S) on the intersection of the plane $\alpha = B_1\alpha$ with the plane ML_1 ; this line rests accordingly on α .

In a system $(1,1)$ the points P lie on a straight line g and the corresponding lines l pass through a point G . The ranges (P) and (B) are projective, hence the plane pencil (m) is projective with the pencil of planes (α) . The image of a $(1,1)$ is therefore a conic σ^2 through M which cuts α . It cuts φ in the point bg and in the point (A_0G, g) .

If G lies on c , σ^2 degenerates into the straight line joining M and the point cg and another straight line of the plane Mg . Also if G lies on b , σ^2 degenerates.

In a system (i, k) the locus of the lines l is a curve of the class i and the points P lie on a curve of the order k . Accordingly k points $B = S$ of the image lie on b , and this curve cuts φ besides in the i points P of which the corresponding lines l pass through A_0 (§ 2). The i elements e of which the lines l pass through D , have their images in M , the k elements for which P lies on c , are represented by points A .

The image of a system (i, k) is therefore a curve of the order $(i + k)$ which passes i times through M , and which has the line α as a k -fold line of intersection.

4. In order to determine the image of a *bilinear null system* $N(1,1)$ I consider the elements e that are represented by points of φ . The points P the null rays of which pass through A_0 , form a conic α_0^2 through A_0 ; this "null curve" forms together with the straight line b the intersection of the image Σ^2 with φ .

The points of the null curve σ^2 corresponding to D , define together with D line elements that have their images in M ; hence Σ^2 has

in M a node of which the cone of tangent lines cuts the plane φ along σ^3 . This surface is accordingly a *cubic monoid* with vertex M .

The elements e that have their null points on c , are represented by points A ; hence Σ^3 contains the line a .

The null point C_0 of c defines the straight line C_0M lying on Σ^3 . Analogously the straight line B_0M passes through the null point B_0 of b , and DM is the image of the element e corresponding to D . On Σ^3 there lie three more straight lines m ; they are the images of three plane pencils belonging to $N(1,1)$. The null system $(1,1)$ has therefore *three singular null points*¹⁾. In each plane through two of the lines m there lies another straight line of Σ^3 ; it is the image of a *singular straight line* of $N(1,1)$, hence a straight line that has each of its points as a null point.

The remaining 10 straight lines are the images of elements e of the monoid that have their null points on a straight line of φ . The null rays of an arbitrary straight line g envelop a conic touching g . The image of the system $(2,1)$ defined in this way is a nodal cubic with double point M which cuts φ in $B = bg$ and in two other points of g .

For the 10 straight lines mentioned the image degenerates into three straight lines; the line r which Σ^3 also has in common with the plane B_0C_0M , forms, together with B_0M and C_0M , the image of a $(2,1)$ the null points of which are projected out of M on r . To the null curves of $N(1,1)$ there correspond twisted cubics of Σ^3 which pass through M and have a as a chord.

5. The image of a null system $N(1, k)$ is a *monoid* Σ^{k+2} with a $(k+1)$ -fold point M . On this monoid lie the straight lines a , b and d besides k straight lines B_0M and k lines C_0M . The remaining $(k+1)(k+2) - 2(k+1)$ straight lines m are images of plane pencils; hence the null system has $(k^2 + k + 1)$ *singular points*²⁾.

As the plane through two of these lines m generally cuts the monoid along a curve of the order k , as a rule an $N(1, k)$ has *no* singular straight lines. As for $n > 3$ a monoid Σ^n generally does not contain any straight lines that do not pass through the vertex, Σ^{k+2} is not the most general monoid of the order $(k+2)$.

The image of a null system $N(i, k)$ where a point P is the null point of i rays l and a straight line l is the null ray of k points,

¹⁾ See my communication on plane linear null systems. These Proceedings, Vol. XV, p. 1165.

²⁾ l. c.

is a surface Σ of the order $(2i+k)$ with an $(i+k)$ -fold point M of which the cone of tangent lines has an i -fold generatrix d .

Σ further contains the i -fold lines a , b and d .

The intersection with φ consists of the i -fold straight line b , and the null curve α_0^{i+k} corresponding to A_0 . Each of the null points of c defines a straight line on Σ ; hence the intersection with the plane μ consists of k lines CM and the i -fold lines a and d . Analogously Σ has the i -fold lines b and d and k lines BM in common with the plane β .

Especially the image of an $N(1,0)$ of which the ∞^2 elements e lie on the rays l of a plane pencil, is a quadratic scroll through the lines a , b , and d . The regulus containing d consists of the images of the elements on the singular null rays.

The null system $N(0,1)$ where any point of a fixed straight line g is the null point of a plane pencil, has apparently for image the points of the plane Mg .

6. If the point S describes a straight line r , the pencil of planes round a becomes projective with the range of points on b and with the range of points on the straight line $g = (Mr, \varphi)$. Hence the straight line l envelops a conic λ^2 touching b and g .

The point $S = r\mu$ is the image of an e formed by $C = cg$ and the line c ; accordingly λ^2 is inscribed in the triangle bcg . The other tangent line out of A_0 cuts g in the point $P = gr$.

Together with b the point $B = bg$ defines an element e that is represented by BM . Analogously $C = cg$ defines an element that has CM for image. The complete image of the system $(2,1)$ defined by g and λ^2 consequently consists of the three straight lines r , BM and CM .

If S describes a twisted curve σ^n resting on a in k points A and passing i times through M , the locus of P is a curve of the order $(n-i)$. As a plane α contains $(n-k)$ points S , a point B is associated to $(n-k)$ points P . By the correspondence between the points B and P a correspondence $(n-i, n-k)$ is established between the rays of a plane pencil chosen arbitrarily in φ . Consequently the lines l envelop a curve (l) of the class $(2n-i-k)$.

The plane μ contains $(n-i-k)$ points S each of which is the image of an element (C, c) ; hence c is an $(n-i-k)$ -fold tangent of (l) . Analogously (l) has the $(n-i)$ -fold tangent b . The complete image of the system $(2n-i-k, n-i)$ consists apparently of the curve σ^n , $(n-i)$ straight lines BM , and $(n-i-k)$ straight lines CM .

7. A surface Σ^n with an i -fold point in M and a k -fold straight line in α is the image of a null system in φ .

A straight line $m = MP$ contains $(n-i)$ points S ; hence P is the null point of $(n-i)$ null rays. The element e of a straight line l are represented by a straight line cutting α ; l has accordingly $(n-k)$ null points. Consequently a null system $N(n-i, n-k)$ corresponds to Σ^n .

Evidently b and c are singular null rays; any point B or C may be considered $(n-i)$ times as the null point of b or c . If Σ^n contains a straight line m (through M) this line is the image of a singular plane pencil.

An arbitrary plane Σ is in particular the image of an $N(1,1)$ for which b and c are singular null rays; the third singular null ray passes through the points $b\Sigma$ and A_0 . The complete image of this null system consists of the planes Σ , μ and β .

The plane φ is the image of the two null systems $N(1,0)$ and $N(0,1)$, which have resp. A_0 as a singular point and b as a singular line.

Chemistry. — “*Conversion of paraffin by heating under pressure in the presence of hydrogen, methane and other gases*”¹). By Prof. H. I. WATERMAN and J. N. J. PERQUIN, Chem. eng. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of January 26, 1924).

The research taken up by us concerning *the scientific and technical significance of Bergius' hydrogenation process* is going to ask still many years of study, while a thorough experimental ability and a highly specialised knowledge of the different kinds of apparatus are necessary. Meanwhile we are already able to give some of the most important results.

Material and working scheme.

The research concerns this time the same kind of paraffin while the scheme of working and the apparatus used have been described in an earlier communication on the decomposition of cottonseed oil²). With the exception of a couple of experiments, where we distilled during the heating, also now no condensor was used.

Excepted in the two experiments just mentioned the heating was done in a closed vessel and consequently no gases were added or blown off during the experiment.

As characteristics for the judgment of the oil we used:

1. *The appearance of the oil, as well as the yield and distillation limits.* Already before we have communicated that by the berginisation of paraffin the oil obtained was clear and light in colour.

2. *The spec. gravity of the oil or of the residue* resulting after the distillation according to ENGLER. In case of hydrogenation the spec. gravity is lower.

3. *The bromine value of the oil or of the fractions* obtained from ENGLER's distillation. Here we want to lay stress upon the fact that

¹) This research is a continuation of a former publication: “The hydrogenation of paraffin by the BERGIUS' Method”. Proceedings Koninklijke Akademie van Wetenschappen, Amsterdam, Vol. XXVI, p. 226 (1923), see also *ibid* Vol. XXVII p. 83. (1924). *Chimie et Industrie*, numéro spécial Mai 1923, p. 200–207.

²) These Proceedings, Vol. XXVII, p. 83 (1924).

the hydrogen consumed is not used in the first place for the elimination of the unsaturation of the gasoline and kerosene formed but probably to improve the residue. An analytical research of this residue (elementary analysis) combined with a determination of the molecular weight, has to bring light into this matter.

4. *The amount of hydrogen consumed.*

This appears entirely from the gasanalysis.

Experimentally it was proved that the apparent consumption of hydrogen, caused by hydrogen dissolving in the oil, was practically of no account.

5. *The quantity of heavy hydrocarbons in the reaction gases.*

In general the lower this quantity the better in technical sense the results are.

6. *The change in pressure during the heating.*

Though the significance of the change in pressure, after the temperature has become constant, has not been definitely settled, a consideration of the pressure curves can give some understanding whether or not we have to do with analogous processes.

A difficulty with this is however that e.g. a relative pressure lowering may be caused by the addition of hydrogen (hydrogenation) or by polymerisation in the gaseous phase¹⁾.

Review of the experiments.

In the table one finds a review of the most important results.

The two experiments in which during the heating gas was blown off were the numbers 58 and 59.

In 58 the reflux cooler was not provided with cooling water while the autoclave was kept closed until the pressure amounted to seven atmospheres²⁾.

Hereafter gas was blown off continuously and the pressure kept constant at seven atmospheres.

Whereas in 59 the autoclave was filled with nitrogen up to seven atmospheres before the beginning of the experiment, therefore the gases could be blown off directly from the beginning of the heating. The conditions in 58 and 59 have some resemblance with those that occur in cracking processes such as the BURTON process³⁾.

¹⁾ N. IPATIEW, Polymerisation der Äthylen-Kohlenwasserstoffe bei hohen Temperaturen und Drucken, Berichte 44, 2978 (1912).

²⁾ A clogging of the tubing caused the pressure to rise to 14 atmospheres during about 10 minutes.

³⁾ H. I. WATERMAN and H. J. W. REUS, The cracking process of BURTON, Rec. Trav. chim. des Pays-Bas 43, (1924), 87.

Of all in the table mentioned experiments only in 58 and 59 a distillate was obtained during the experiment. In 58 the distillate became solid at 0°C ., the bromine value being very high 76.5, while the residue in the autoclave was liquid and had a bromine value of 24.6.

In 59 the bromine value of the distillate was 82.7 and of the residue 39.7. The residue contained gum-like constituents. For further research a portion of the distillate and residue of 58 and 59 were mixed in the proportion by weight as they were formed in the experiments.

Although also in 58 and 59, as well as in all other experiments little or no cokeformation occurred, the oils of experiment 58 and 59, as far as their bromine value was concerned, and the gases on account of their great percentage of heavy hydrocarbons, stood far back by all other experiments.

Especially the difference was great with those experiments, where, according to BERGIUS, was heated with hydrogen under high pressure, namely in 55 and 57 but especially with experiment 52 where a very high hydrogen pressure was reached.

In 52 not less than at least 34 Liters of hydrogen have been consumed, in 55 and 57 more than 20 Liters. If we compare this with experiment 60 and 61, then it appears that in this connection *a high hydrogen pressure was indeed necessary*. For the oils of experiment 60 and 61 have a higher bromine value and a higher spec. gravity, while it appears from the gasanalysis of experiment 61 (the gas of experiment 60 was lost) that practically no hydrogen had been consumed; 7.6 Liters hydrogen were added and 7.7 Liters were recovered. In cracking experiment 56 which can be compared with these 1.3 Liters hydrogen were formed. *Neither does hydrogen in status nascens offer any improvements* in this respect as appears from experiments 62 and 63 where mixtures of CO and H_2O were used ¹⁾.

In these experiments the CO_2 and hydrogen, formed according to the equation. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, were present in the reaction gases in nearly equivalent quantities, namely 6.6 and 7.1 Liters CO_2 , with respectively 6.4 and 7.6 Liters hydrogen.

In the corresponding experiment 56, already mentioned, 1.3 Liters hydrogen were formed.

¹⁾ This confirms a research by H. I. WATERMAN and F. KORTLANDT: "The treatment of Mexican asphalt and paraffin wax by heating under high pressure with sodiumformate and with carbonmonoxide and water respectively, Rec. trav. chim. des Pays-Bas 43 p. 249, (1924).

As in 60 and 61, it appears that in 62 and 63 no important hydrogen consumption took place. In this respect there is no difference for paraffin between hydrogen under low pressure and hydrogen formed during the experiment by the reduction of water by CO.

An indifferent gas under high pressure, such as nitrogen (64) and high pressure technical methane (53 and 54) neither has a favourable influence.

We find that in 64 the amount of nitrogen added remained unchanged, while in 54 the total volume of hydrocarbons in the reaction gases was only slightly changed. Experiment 53 seems to point to a, may be slightly pronounced, decrease. The results of the gasanalysis (percentage N_2), the low pressure after complete cooling and the low yield of gas, however, point to a small leak that probably arose during the cooling. Furthermore one sees that in 54 the hydrogen present in the methane as an impurity is recovered after the experiment.

If we compare the experiments with hydrogen under high pressure (52, 55 and 57), hydrogen under low pressure (60 and 61), methane under high pressure (54), hydrogen in status nascens ($CO + H_2O$, 62 and 63) nitrogen under high pressure (64) and simple heating in a closed autoclave only under the pressure of the gases that develop during the heating (56) then it appears that:

1. *The yield of oil, resp. gasoline, kerosene and residue is practically the same in all these experiments.*

From this appears that the yield of gas ought to be practically the same too.

2. *Experiment 52, 55, and 57 with hydrogen under high pressure distinguish themselves in a favourable sense, namely:*

A. a better appearance and a lower spec. gravity of the oil.

B. a lower bromine value (addition) of the gasoline and kerosene.

If we compare 60 and 61, 53 and 54, 62 and 63, 64 and 56 on the one side, with 58 and 59 on the other, in the latter two experiments distillation took place during the heating while the pressure was kept constant at seven atmospheres, then it appears that:

a. the yield of gas was greater in 58 and 59. The yield of oil is consequently lower, even if (in 58 and 59) there had not been any losses ¹⁾.

b. The gas of 58 and 59 contained much heavy hydrocarbons.

¹⁾ One has to reckon with the fact that in 58 the experiment was started without any pressure while experiment 59 was started after the nitrogen pressure amounted seven atmospheres.

| No. | Time required to reach the temp (min.) | Duration of the exp. after the reaction temp. has been reached (min.) | Reaction temperature (average) | Pressure at the beginning of the experiment KG/cm ² | Max. pressure during the experiment | Pressure after complete cooling | Products obtained | | | Spec. grav. of the oil at 15° | Distillation of the poured out (ENG) | | |
|-----|--|---|--------------------------------|--|-------------------------------------|---------------------------------|-------------------|------|--------|-------------------------------|---|-----------------------|--------------------|
| | | | | | | | In Grammes | | Liters | | Gasoline ³⁾ (up to 220°) Gr. | Kerosene 220—300° Gr. | Residue > 300° Gr. |
| | | | | | | | Oil | Gas | Gas | | | | |
| 52 | 35 | 60 | 450° | 110 | 219 | 87 | 177 | 27.5 | 93 | 0.735 | 98.2 | 35.0 | 43.8 |
| 55 | 40 | 60 | 450° | 60 | 142 | 50 | 172 | 33.8 | 61 | 0.745 | 109.2 | 31.8 | 31.0 |
| 57 | 25 | 60 | 452° | 60 | 140 | 50 | 173 | 32.4 | 60.5 | 0.744 | 104.4 | 34.2 | 34.4 |
| 60 | 30 | 60 | 451° | 7 | 65.5 | — | 173 | — | — | 0.769 | 100.2 | 33.6 | 39.2 |
| 61 | 29 | 60 | 450° | 7 | 59 | 13 | 177 | 17.5 | 19.5 | 0.769 | 92.0 | 35.6 | 49.4 |
| 53 | 40 | 60 | 450° | 75 | 189.5 | 59 | 174 | 75.2 | 87 | 0.769 | 97.8 | 34.2 | 42.0 |
| 54 | 48 | 60 | 451° | 60 | 162 | 61 | 174 | 77.4 | 91 | 0.772 | 99.1 | 35.0 | 39.9 |
| 62 | 31 | 60 | 451° | 23 | 117 | 32 | 176 ¹⁾ | 47.5 | 41 | 0.767 | 96.1 | 36.6 | 43.3 |
| 63 | 40 | 60 | 450° | 23 | 116 | 31.5 | 180 ¹⁾ | 51.4 | 43.8 | 0.765 | 97.7 | 35.9 | 46.4 |
| 64 | 33 | 60 | 451° | 60 | 172.5 | 66 | 176 | 96.7 | 80 | 0.768 | 98.3 | 34.7 | 43.1 |
| 56 | 32 | 60 | 449° | 0 | 49.5 | 8.8 | 171 | 23.2 | 18 | 0.763 | 95.6 | 32.0 | 43.4 |
| 58 | 30 | 60 | 450° | 0 | 7 | 0 | 133 ²⁾ | 30 | 19.5 | 0.750 | 85.3 | 23.0 | 24.7 |
| 59 | 31 | 60 | 450° | 7 | 7 | 0 | 161 ²⁾ | 44.6 | 29.5 | 0.773 | 77.2 | 27.1 | 56.9 |

¹⁾ Saturated with water.

²⁾ In these experiment oil losses were great.

³⁾ Including losses caused by evaporation during the distillation.

⁴⁾ The oil obtained is here a mixture of distillate and oil poured out of the autoclave in the true proportion by weight.

AFFIN (200 Gr.).

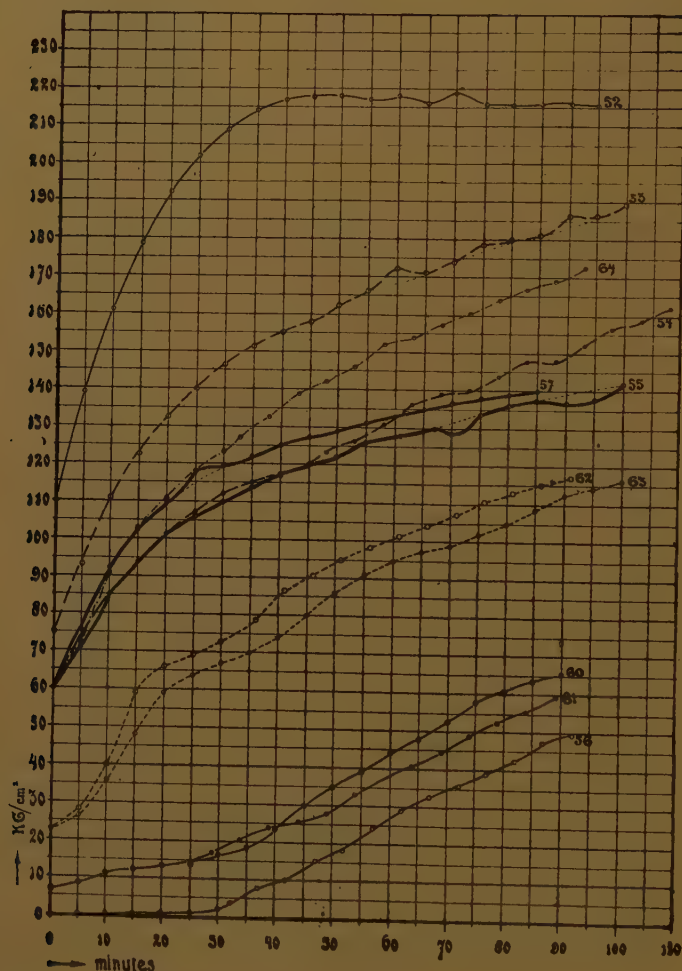
| Initial value (before experiment). | | Liters of gas added before the beginning of the experiment 5) | | | | | | | Liters of gas recovered after the experiment 5) | | | | | | | |
|------------------------------------|----------|---|---------------------|----------------|------|----------------|---|-----------------------|---|--------------------|----------------|------|----------------|---|-----------------------|--|
| Gasoline | Kerosene | CO ₂ | Heavy hydrocarbons. | O ₂ | CO | H ₂ | Other hydrocarbons (CH ₄ a.o.) | N ₂ (rest) | CO ₂ | Heavy hydrocarbons | O ₂ | CO | H ₂ | Other hydrocarbons (CH ₄ a.o.) | N ₂ (rest) | |
| 9.3 | 9.5 | — | — | 0.3 | — | 113.2 | — | — | — | 0.9 | — | — | 79.3 | 9.3 | 3.5 | Hydrogen under high pressure |
| 3.4 | 13.7 | — | — | 0.1 | — | 63.9 | — | — | — | 1.3 | 0.6 | — | 40.4 | 16.4 | 2.3 | |
| 3.9 | 13.6 | — | — | 0.1 | — | 63.9 | — | — | — | 1.6 | 0.2 | — | 41.3 | 15.7 | 1.7 | |
| 4.5 | 15.7 | — | — | — | — | 7.6 | — | — | The gas of this experiment was lost | | | | | | | Hydrogen under low pressure |
| 3.3 | 16.8 | — | — | — | — | 7.6 | — | — | — | 1.4 | 0.2 | — | 7.7 | 9.3 | 0.9 | |
| 5.9 | 15.9 | 0.6 | 3.5 | 1.2 | 1.0 | 4.0 | 77.3 | 9.0 | 1.3 | 2.5 | 0.3 | 0.8 | 5.1 | 74.6 | 2.4 | Methane under high pressure |
| 5.6 | 14.4 | 0.4 | 2.6 | 1.0 | 0.8 | 3.0 | 58.9 | 6.8 | — | 2.1 | 0.8 | 1.0 | 2.8 | 77.0 | 7.3 | |
| 7.8 | 16.5 | — | — | 0.1 | 23.5 | 0.4 | not determined | not determined | 6.6 | 1.3 | 0.3 | 14.5 | 6.4 | 10.3 | 1.6 | CO + H ₂ O in equivalent quantities |
| 7.9 | 16.5 | — | — | 0.1 | 23.0 | 0.4 | not determined | not determined | 7.1 | 1.3 | 0.2 | 15.8 | 7.6 | 10.7 | 0.9 | |
| 5.4 | 16.1 | — | — | 1.9 | — | — | — | 65.1 | 1.0 | 0.8 | 0.3 | — | 1.4 | 11.0 | 65.5 | Nitrogen under high pressure |
| 5.5 | 16.9 | — | — | — | — | — | — | — | — | 3.6 | 0.2 | — | 1.3 | 11.7 | 1.3 | |
| 5.4 | 29.7 | — | — | — | — | — | — | — | 0.2 | 6.8 | 0.3 | 0.1 | 1.2 | 8.0 | 2.9 | Cracking under constant pressure (7 atm.) |
| 3.0 | 26.5 | — | — | — | — | — | — | 14.0 | 0.1 | 5.9 | 0.2 | — | 1.0 | 6.8 | 15.5 | |

Heating in a closed vessel

5) Here has not been reckoned with the gas present in the autoclave before and after the experiment (about 1 Liter). In all experiments excepted in 56 the autoclave was forced up first and then blown off and the gas measured after which the autoclave was forced up again, consequently practically no air is present. In 58 the air was driven out by nitrogen before the experiment.

c. The bromine value of the oil of 58 and 59 is extraordinary high.

The heating in a closed autoclave or the heating in one which has been filled before with a little hydrogen, methane or nitrogen under high pressure or with $\text{CO} (+\text{H}_2\text{O})$, and by which pressures of 50 atmospheres and higher were reached during the heating, is consequently better than a heating by which one keeps the pressure constant at 7 atmospheres and one distills in the meantime.



A consideration of the graphical representation of the change in pressure in 52, 55 and 57, 60, 61, 53, 54, 62, 63, 64 and 56 shows that, with the exception of the three berginisation experiments 52, 55 and 57, the pressure increases considerably even after the temperature has become constant.

There were hydrogen has been consumed (52, 55 and 57) the

curve is absolutely different, the pressure curve becomes nearly horizontal in 52 where most hydrogen has been consumed.

As explained before, we cannot enter into an explanation of the course of the pressure curves because a clear understanding of the kind of reaction products and of the chemical reactions taking place during the process fails at present. Finally we wish to express our thanks to Mr. J. A. BEUKERS, chemical engineer, for his assistance during the course of this research.

Delft,

*Laboratory for Chemical Technology
of the Technical University.*

Physiology. — "*On the Mode of Action of Insulin*". By Prof. B. SJOLLEMA and L. SEEKLES. (Communicated by Prof. A. A. HYMANS VAN DEN BERGH).

(Communicated at the meeting of January 29, 1924).

An inquiry into the nature of the active principle of the medicine prepared from the pancreas, which is now generally known by the name of "insulin", or "glucopyron", may be initiated by physiological experiments with a view to fix upon substances that are analogous to insulin as to their mode of action.

Since for several reasons a chemical inquiry offers but little chance of success, unless indications have been obtained, by the above orientation-method, we followed the latter course.

One of the points we studied, was the question whether calcium-salts and insulin act antagonistically. In these experiments we determined the bloodsugar after the method of FOLIN and WU. The insulin had been prepared by ourselves from the cow's pancreas by a modified method.

Many injections of this preparation were administered to several rabbits. The result was that 3 mgrs. yielded an average decrease of 114 mgrs. of glucose per 100 c.c. of blood¹⁾. When 3 mgrs. of this preparation were injected together with 600 mgrs. of calcium-chloride per k.g. bodyweight, the bloodsugar-lowering action of the insulin was inhibited or nearly so, the mean depression was then only 4,5 mgrs. instead of 114 mgrs. per 100 c.c. of blood.

The calciumchloride was calculated as CaCl_2 , but the crystalline salt was used.

The six experiments in which the combined action of the calcium-chloride and the insulin was examined gave the following results:

—0,052; —0,024; —0,007; +0,006; +0,014; +0,037 on an average —0,0045 grms depression per 100 c.c. of blood.

Once a quantity of Calciumacetate, equivalent to the above quantum of Calciumchloride was injected together with the insulin. The bloodsugar depression amounted to no more than 0.013 grms. The antagonistic action must, therefore, be ascribed to the Calcium.

¹⁾ The injected dosis amounted to about $4\frac{1}{2}$ rabbit-units. This unit is $\frac{1}{3}$ of the dosis required to lower the bloodsugar-content in a rabbit of about 2 K.G. to +0,045 %.

Twice the above quantum of Calciumchloride was injected without insulin. The bloodsugar-content remained approximately constant. Once it was augmented with 0.015 grm and once it was lowered with 0.003 grm per 100 c.c. of blood. Three times we also tried to neutralize the normal effect of the insulin with less Calciumchloride, namely with $\frac{1}{6}$ of the above quantity.

The dosis of insulin injected in these last experiments amounted to 3 rabbit-units. In two of these experiments the bloodsugar-content was lowered resp. with 0.037 and 0.062 grms and in the third it increased with 0.008 grms per 100 c.c. of blood. So the average decrease was 0.0033 grms while without Calciumchloride it would have been about 0.080 grms. This clearly proves that this small quantity of salt has counteracted the insulin.

Besides for the study of the nature of the active principle of insulin the result we obtained with Calciumchloride may also be of value for the therapeutic application of this medicine.

Whether in the observed action of Calcium the disturbance of the ions-equilibrium plays a rôle, and whether the salts of other metals, present in the blood, exhibit analogous actions, are problems we are still occupied in examining.

In view of several of our results we intend to compare the action of cyanamid and of different derivatives from guanidine, with the action of insulin, as well with regard to the influence on the sugar-metabolism as concerning the effect on the cell-activity and on the amount of phosphoric acid, calcium and sodium bicarbonate, contained in the blood.

Mathematics. — “*Euler’s constant and natural numbers*”. By Prof.
J. C. KLUYVER.

(Communicated at the meeting of February 23, 1924).

The first representation of EULER’S constant C as the limit of a rational expression of natural numbers is due to Vacca, who in 1910 arrived at the remarkable result

$$C = \left(\frac{1}{2} - \frac{1}{3}\right) + 2\left(\frac{1}{4} - \frac{1}{5} + \frac{1}{6} - \frac{1}{7}\right) + \\ + 3\left(\frac{1}{8} - \frac{1}{9} + \frac{1}{10} - \dots - \frac{1}{15}\right) + 4\left(\frac{1}{16} - \frac{1}{17} + \frac{1}{18} - \dots - \frac{1}{31}\right) + \dots$$

The convergence of this series is not disturbed, if we remove the brackets and write

$$C = \sum_2^{\infty} \frac{(-1)^k [^2 \log k]}{k},$$

where $[x]$ stands for the integer part of the number x . At first sight we might think that the number 2 as the base of the logarithms plays a predominant part in the construction of the series, but such is not the case. In fact, selecting an arbitrary integer a and putting β_k equal to $a-1$ or to -1 , according as k is, or is not a multiple of a , we have in quite the same way

$$C = \sum_a^{\infty} \frac{\beta_k [^a \log k]}{k}.$$

From these expansions it is evident that C is intimately connected with the natural numbers, and the consideration of another expression of C , that I am going to deduce, suggests anew the existence of this connexion. From the known formula

$$\frac{\Gamma'}{\Gamma}(1+a) + C = \int_0^1 \frac{1-x^a}{1-x} dx = \int_0^1 \frac{1-(1-y)^a}{y} dy = \int_0^1 \frac{dy}{y} \sum_1^{\infty} (-1)^{h-1} a_h y^h$$

we obtain at once by integrating with respect to a between the limits 0 and 1

$$C = \sum_1^{\infty} \frac{\alpha_h}{h},$$

where the coefficients α_h are determined by the equation

$$\alpha_h = (-1)^{h-1} \int_0^1 a_h da = + \frac{1}{h} \int_0^1 a \left(1 - \frac{a}{1}\right) \left(1 - \frac{a}{2}\right) \left(1 - \frac{a}{3}\right) \dots \left(1 - \frac{a}{h-1}\right) da.$$

Obviously the numbers α_h are positive and rational and it is seen that the sequence (α_h) is decreasing to the limit zero. In order to evaluate α_h , we observe that the equation

$$\int_0^1 (1-y)^a da = \frac{y}{\log \frac{1}{1-y}} = 1 - \sum_1^{\infty} \alpha_h y^h$$

leads to the identity

$$1 = \left(1 - \sum_1^{\infty} \alpha_h y^h\right) \sum_1^{\infty} \frac{y^{h-1}}{h}.$$

Hence the coefficients α_h are found from the equations

$$\frac{1}{2} = \frac{\alpha_1}{1},$$

$$\frac{1}{3} = \frac{\alpha_1}{2} + \frac{\alpha_2}{1},$$

$$\frac{1}{4} = \frac{\alpha_1}{3} + \frac{\alpha_2}{2} + \frac{\alpha_3}{1},$$

$$\frac{1}{5} = \frac{\alpha_1}{4} + \frac{\alpha_2}{3} + \frac{\alpha_3}{2} + \frac{\alpha_4}{1},$$

.

As the sequence (α_h) is decreasing, we must have

$$\alpha_h < \frac{1}{(h+1) \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{h} \right)} < \frac{1}{h \log h},$$

therefore we conclude that the terms of the somewhat irregular expansion

$$C = \sum_1^{\infty} \frac{\alpha_h}{h} = \frac{1}{2} + \frac{1}{24} + \frac{1}{72} + \frac{19}{2880} + \frac{3}{800} + \frac{863}{362880} + \frac{275}{169344} + \dots$$

are less than the corresponding terms of the series $\sum_2 \frac{1}{h^2 \log h}$. Its convergence may be slow, but it converges more rapidly than Vacca's expansion.

The above result can be put into another form. Writing

$$C = \lim_{h \rightarrow \infty} \left(\frac{\alpha_1}{1} + \frac{\alpha_2}{2} + \frac{\alpha_3}{3} + \dots + \frac{\alpha_h}{h} \right),$$

and joining this equation to the equations satisfied by the coefficients α_h , we obtain by solving for C

$$C = - \lim_{h \rightarrow \infty} \begin{vmatrix} 0 & \frac{1}{1} & \frac{1}{2} & \frac{1}{3} & \dots & \frac{1}{h} \\ \frac{1}{2} & \frac{1}{1} & 0 & 0 & \dots & 0 \\ \frac{1}{3} & \frac{1}{2} & \frac{1}{1} & 0 & \dots & 0 \\ \frac{1}{4} & \frac{1}{3} & \frac{1}{2} & \frac{1}{1} & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \frac{1}{h+1} & \frac{1}{h} & \frac{1}{h-1} & \frac{1}{h-2} & \dots & \frac{1}{1} \end{vmatrix}$$

and thus we have again deduced a rational expression of the natural numbers, that converges to the mysterious constant C .

For purposes of numerical computation these expansions of C are not convenient, and a more serviceable relation is obtained as follows.

If we integrate with respect to a between the limits 0 and 1 both sides of the equation

$$\frac{\Gamma'}{\Gamma}(a + \mu + 1) + C = \int_0^1 \frac{dy}{y} \{1 - (1-y)^\mu\} + \int_0^1 dy \sum_1^\infty (-1)^{h-1} a_h y^{h-1} (1-y)^\mu,$$

we will find

$$C = \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{\mu} \right) - \log(\mu + 1) + \Gamma(1 + \mu) \sum_1^\infty \frac{\alpha_h}{h(h+1)(h+2)\dots(h+\mu)}.$$

Now in this expansion an irrational term occurs, but taking for instance $\mu = 5$, this formula gives the numerical value of C with tolerable accuracy by using only the first six terms of the series at the righthandside.

Mathematics. — “The numbers of STIRLING expressed by definite integrals”. By Prof. W. KAPTEYN.

(Communicated at the meeting of February 23, 1924).

1. If $x(x+1)\dots(x+n)$ be expanded in a series of ascending powers of x

$$C_{n+1}^0 x^{n+1} + C_{n+1}^1 x^n + \dots + C_{n+1}^n x$$

the coefficients C_{n+1}^r are called STIRLING's numbers of the first kind.

Equating both forms and dividing by x we get

$$n!(1+x)\left(1+\frac{x}{2}\right)\dots\left(1+\frac{x}{n}\right) = C_{n+1}^n + C_{n+1}^{n-1}x + \dots + C_{n+1}^0 x^n.$$

Thus we have

$$C_{n+1}^n = n!$$

$$C_{n+1}^{n-1} = n! \sum \frac{1}{\alpha}$$

$$C_{n+1}^{n-2} = n! \sum \frac{1}{\alpha\beta}$$

.

where $\sum \frac{1}{\alpha}$, $\sum \frac{1}{\alpha\beta}$, ... represent the sums of all different products

of the quantities $\frac{1}{1}, \frac{1}{2}, \dots, \frac{1}{n}$ one by one; two by two, etc.

2. The first sum may immediately be written in the form of a definite integral, for

$$\sum_1^n \frac{1}{\alpha} = 1 + \frac{1}{2} + \dots + \frac{1}{n} = \int_0^1 \frac{1-x^n}{1-x} dx \dots \dots \dots (1)$$

The second sum may be reduced to the first, for

$$S_n = \sum \frac{1}{\alpha\beta} = S_{n-1} + \frac{1}{n} \sum \frac{1}{\alpha}$$

or

$$S_n = S_{n-1} + \frac{1}{n} \int_0^1 \frac{1-y^{n-1}}{1-y} dy.$$

Hence

$$S_{n-1} = S_{n-2} + \int_0^1 \frac{1-y^{n-2}}{1-y} dy$$

$$S_{n-2} = S_{n-3} + \frac{1}{n-2} \int_0^1 \frac{1-y^{n-3}}{1-y} dy$$

.

$$S_3 = S_1 + \frac{1}{3} \int_0^1 \frac{1-y^2}{1-y} dy$$

$$S_1 = \frac{1}{2} \int_0^1 \frac{1-y}{1-y} dy$$

and therefore

$$S_n = \int_0^1 \frac{dy}{1-y} \left\{ \frac{1-y}{2} + \frac{1-y^2}{3} + \dots + \frac{1-y^{n-1}}{n} \right\}.$$

Now we know that

$$\frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n} = \int_0^1 \frac{x(1-x^{n-1})}{1-x} dx = \int_0^1 P dx$$

$$\frac{y}{2} + \frac{y^2}{3} + \dots + \frac{y^{n-1}}{n} = \frac{1}{y} \int_0^y \frac{x(1-x^{n-1})}{1-x} dx = \frac{1}{y} \int_0^y P dx$$

thus we may write

$$S_n = \int_0^1 \frac{dy}{1-y} \int_0^1 P dx - \int_0^1 \frac{dy}{y(1-y)} \int_0^y P dx$$

or

$$S_n = \int_0^1 \frac{dy}{1-y} \int_y^1 P dx - \int_0^1 \frac{dy}{y} \int_0^y P dx.$$

By interchanging the order of the integrations we obtain

$$S_n = \int_0^1 P dx \int_0^x \frac{dy}{1-y} - \int_0^1 P dx \int_x^1 \frac{dy}{y}$$

or finally

$$S_n = \int_0^1 P \lg \frac{x}{1-x} dx \left(P = \frac{x(1-x^{n-1})}{1-x} \right) \dots \dots (2)$$

3. Reducing the third sum to the second we get in the same way

$$S_n = \sum_{\alpha\beta\gamma}^n \frac{1}{\alpha\beta\gamma} = S_{n-1} + \frac{1}{n} \sum^{n-1} \frac{1}{\alpha\beta}$$

or, introducing the value (2)

$$S_n = S_{n-1} + \frac{1}{n} \int_0^1 \frac{y(1-y^{n-2})}{1-y} \lg \frac{y}{1-y} dy$$

which leads to

$$S_n = \int_0^1 \frac{y}{1-y} \lg \frac{y}{1-y} dy \left[\frac{1}{3} (1-y) + \frac{1}{4} (1-y^2) + \dots + \frac{1}{n} (1-y^{n-2}) \right].$$

Here we have

$$\frac{1}{3} + \frac{1}{4} + \dots + \frac{1}{n} = \int_0^1 \frac{x^2(1-x^{n-2})}{1-x} dx = \int_0^1 P dx$$

$$\frac{y}{3} + \frac{y^2}{4} + \dots + \frac{y^{n-2}}{n} = \frac{1}{y^2} \int_0^y \frac{x^2(1-x^{n-2})}{1-x} dx = \frac{1}{y^2} \int_0^y P dx$$

thus

$$S_n = \int_0^1 \frac{y}{1-y} \lg \frac{y}{1-y} dy \left[\int_0^1 P dx - \frac{1}{y^2} \int_0^y P dx \right]$$

or

$$S_n = \int_0^1 \frac{y}{1-y} \lg \frac{y}{1-y} dy \int_y^1 P dx - \int_0^1 \frac{1+y}{y} \lg \frac{y}{1-y} dy \int_0^y P dx.$$

By interchanging the order of the integrations we obtain

$$S_n = \int_0^1 P dx \left[\int_0^x \frac{y}{1-y} \lg \frac{y}{1-y} dy - \int_x^1 \frac{1+y}{y} \lg \frac{y}{1-y} dy \right]$$

which may be reduced to

$$S_n = \frac{1}{2} \int_0^1 P dx \left[\lg^2 \frac{x}{1-x} - \frac{\pi^2}{3} \right] \left(P = \frac{x^2(1-x^{n-2})}{1-x} \right) \quad (3)$$

4. In the same way the following results will be found

$$\sum_{\alpha\beta\gamma\delta}^n \frac{1}{\alpha\beta\gamma\delta} = \frac{1}{3!} \int_0^1 P dx \left[\lg^3 \frac{x}{1-x} - \pi^2 \lg \frac{x}{1-x} \right] \left(P = \frac{x^3(1-x^{n-3})}{1-x} \right) \quad (4)$$

$$\sum_{\alpha\beta\gamma\delta\epsilon}^n \frac{1}{\alpha\beta\gamma\delta\epsilon} = \frac{1}{4!} \int_0^1 P dx \left[\lg^4 \frac{x}{1-x} - 2\pi^2 \lg^2 \frac{x}{1-x} + \frac{\pi^4}{5} \right] \left(P = \frac{x^4(1-x^{n-4})}{1-x} \right) \quad (5)$$

from which we conclude by induction

$$\sum_{\alpha\beta\ldots\lambda}^n \frac{1}{\alpha\beta\ldots\lambda} = \frac{1}{p!} \int_0^1 \frac{x^p(1-x^{n-p})}{1-x} \left[\lg^p - \frac{p \cdot p-1}{3!} \pi^2 \lg^{p-2} + \right. \\ \left. + \frac{p \cdot p-1 \cdot p-2 \cdot p-3}{5!} \pi^4 \lg^{p-4} \ldots \right] dx$$

assuming that the number of the different letters $\alpha\beta\ldots\gamma$ is $p+1$, and omitting the argument $\frac{x}{1-x}$ of the logarithms.

The resulting equation is therefore, if $n > p$

$$C_{n+1}^{n-p-1} = \frac{n!}{p!} \int_0^1 \frac{x^p(1-x^{n-p})}{1-x} \left[\lg^p - \frac{p \cdot p-1}{3!} \pi^2 \lg^{p-2} + \ldots \right] dx \quad (6)$$

where the last term between the parentheses is

$(-1)^{\frac{p}{2}} \frac{\pi^p}{p+1}$ if p is even, and $(-1)^{\frac{p-1}{2}} \pi^{p-1} \lg$ if p is odd.

5. In order to prove exactly the preceding result (6) we want some auxiliary theorems, which we now will examine.

Theorem 1.

$$\int_0^1 \left[\lg^p - \frac{p \cdot p-1}{3!} \pi^2 \lg^{p-2} + \frac{p \cdot p-1 \cdot p-2 \cdot p-3}{5!} \pi^4 \lg^{p-4} - \dots \right] dx = 0 \quad (7)$$

Let $\frac{x}{1-x} = e^{-y}$, then

$$a_{2m} = \int_0^1 \lg^{2m} \frac{x}{1-x} dx = \int_{-\infty}^{\infty} \frac{y^{2m} e^y}{(e^y + 1)^2} dy = (2^{2m} - 2) B_m \pi^{2m}$$

$$a_{2m+1} = 0.$$

Therefore the theorem is proved if p is odd, and also when p is even, for then it reduces to a known relation between Bernouillian numbers.

Theorem 2.

$$\int_0^1 x^n \left[\lg^p - \frac{p \cdot p-1}{3!} \pi^2 \lg^{p-2} + \dots \right] dx = 0 \quad (n < p) \quad (8)$$

Integrating by parts, we get

$$\begin{aligned} \int_0^1 \left[(n+1) x^n - (n+2) x^{n+1} \right] \left[\lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 \lg^{p-1} + \dots \right] dx = \\ = \left[\left(x^{n+1} - x^{n+2} \right) \left(\lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 \lg^{p-1} + \dots \right) \right]_0^1 \\ - (p+1) \int_0^1 x^n \left[\lg^p - \frac{p \cdot p-1}{3!} \pi^2 \lg^{p-2} + \dots \right] dx \end{aligned}$$

or, because $\left[x(1-x) \lg^r \frac{x}{1-x} \right]_0^1 = 0$

$$\int_0^1 \left[(n+1)x^n - (n+2)x^{n+1} \right] \left[lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 lg^{p-1} + \dots \right] dx =$$

$$= -(p+1) \int_0^1 x^n \left[lg^p - \frac{p \cdot p-1}{3!} \pi^2 lg^{p-2} + \dots \right] dx.$$

Assuming in the first place $n=0$, this formula reduces to

$$\int_0^1 x \left[lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 lg^{p-1} + \dots \right] dx = 0.$$

Putting secondly $n=1$, the same formula gives

$$\int_0^1 x^2 \left[lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 lg^{p-1} + \dots \right] dx = 0.$$

Pursuing in the same way, and substituting finally $n=p-1$, we obtain

$$\int_0^1 x^p \left[lg^{p+1} - \frac{p+1 \cdot p}{3!} \pi^2 lg^{p-1} + \dots \right] dx = 0.$$

which proves the theorem.

Theorem 3.

$$\int_0^1 x^n \left[lg^p - \frac{p \cdot p-1}{3!} \pi^2 lg^{p-2} + \dots \right] dx =$$

$$= \frac{p}{n+1} \int_0^1 \frac{1-x^n}{1-x} \left[lg^{p-1} - \frac{p-1 \cdot p-2}{3!} \pi^2 lg^{p-3} + \dots \right] dx \quad (9).$$

Integrating by parts, we have evidently

$$\int_0^1 \left[nx^{n-1} - (n+1)x^n \right] lg^p dx = -p \int_0^1 x^{n-1} lg^{p-1} dx.$$

Replacing n successively by $n-1, n-2, \dots, 1$ and adding the results, we obtain

$$\int_0^1 x^n lg^p dx = \frac{p}{n+1} \int_0^1 \frac{1-x^n}{1-x} lg^{p-1} dx + \frac{1}{n+1} \int_0^1 lg^p dx. \quad (10)$$

Therefore also

$$\int_0^1 x^n l g^{p-2} dx = \frac{p-2}{n+1} \int_0^1 \frac{1-x^n}{1-x} l g^{p-3} dx + \frac{1}{n+1} \int_0^1 l g^{p-2} dx$$

$$\int_0^1 x^n l g^{p-4} dx = \frac{p-4}{n+1} \int_0^1 \frac{1-x^n}{1-x} l g^{p-5} dx + \frac{1}{n+1} \int_0^1 l g^{p-4} dx \text{ etc.}$$

Multiplying these equations respectively with

$$1, -\frac{p \cdot p-1}{3!} \pi^2, \frac{p \cdot p-1 \cdot p-2 \cdot p-3}{5!} \pi^4, \text{ etc.}$$

and adding, the theorem is proved.

6. Returning to the equation (6) we may now give an exact proof in the following way.

According to (6) we have

$$C_{n+1}^{n-p-1} - n C_n^{n-p-2} = \frac{n!}{p!} \int_0^1 x^{n-1} \left[l g^p - \frac{p \cdot p-1}{3!} \pi^2 l g^{p-2} + \dots \right] dx$$

where the second member by means of Theorem 3 may be written

$$\frac{n-1!}{p-1!} \int_0^1 \frac{1-x^{n-1}}{1-x} \left[l g^{p-1} - \frac{p-1 \cdot p-2}{3!} \pi^2 l g^{p-3} + \dots \right] dx$$

or, if we subtract from it, as we know from Theorem 2

$$\frac{n-1!}{p-1!} \int_0^1 \frac{1-x^{p-1}}{1-x} \left[l g^{p-1} - \frac{p-1 \cdot p-2}{3!} \pi^2 l g^{p-3} + \dots \right] dx = 0$$

$$C_{n+1}^{n-p-1} - n C_n^{n-p-2} =$$

$$= \frac{n-1!}{p-1!} \int_0^1 \frac{x^{p-1} (1-x^{n-p})}{1-x} \left[l g^{p-1} - \frac{p-1 \cdot p-2}{3!} \pi^2 l g^{p-3} + \dots \right] dx.$$

Here the second member, as follows from (6) is

$$C_n^{n-p-1}.$$

In this way the equation (6) leads to a known relation between the numbers of STIRLING of the first kind, which proves that this equation is valid generally.

If to (6) we add

$$0 = \frac{n!}{p!} \int_0^1 \frac{1-x^n}{1-x} \left[lg^p - \frac{p \cdot p-1}{3!} \pi^2 lg^{p-2} + \dots \right] dx$$

this equation may also be written

$$C_{n+1}^{n-p-1} = \frac{n!}{p!} \int_0^1 \frac{1-x^n}{1-x} \left[lg^p - \frac{p \cdot p-1}{3!} \pi^2 lg^{p-2} + \dots \right] dx \quad (11)$$

7. Before considering the STIRLING numbers of the second kind, we wish to show how the integrals we met with in the preceding part, may be determined directly.

First case $n \leq p$.

Putting successively $n = 1, 2, 3 \dots$ in the equation

$$(n+1) \int_0^1 x^n lg^p dx = p \int_0^1 \frac{1-x^n}{1-x} lg^{p-1} dx + a_p \dots \quad (10)$$

we obtain

$$2! \int_0^1 x lg^p dx = p a_{p-1} + a_p$$

$$3! \int_0^1 x^2 lg^p dx = p \cdot p-1 a_{p-2} + 3 p a_{p-1} + 2 a_p$$

$$4! \int_0^1 x^3 lg^p dx = p \cdot p-1 \cdot p-2 a_{p-3} + 6 p \cdot p-1 a_{p-2} + 11 p a_{p-1} + 6 a_p$$

$$5! \int_0^1 x^4 lg^p dx = p \cdot p-1 \cdot p-2 \cdot p-3 a_{p-4} + 10 p \cdot p-1 \cdot p-2 a_{p-3} + \\ + 35 p \cdot p-1 \cdot a_{p-2} + 50 p \cdot a_{p-1} + 24 a_p$$

The coefficients in the second members of these equations are easily recognised as the STIRLING numbers

$$\begin{aligned} C_2^0 C_2^1 \\ C_3^0 C_3^1 C_3^2 \\ C_4^0 C_4^1 C_4^2 C_4^3 \\ C_5^0 C_5^1 C_5^2 C_5^3 C_5^4 \\ \dots \end{aligned}$$

$$\int_0^1 x^n \lg^2 dx = \frac{3}{n+1} \int_0^1 (1+x) \lg^2 dx + \frac{3}{n+1} \int_0^1 (x^2 + x^3 + \dots x^{n-1}) \lg^2 dx +$$

$$+ \frac{1}{n+1} a_1$$

where according to (12)

$$\int_0^1 (1+x) \lg^2 dx = C_1^0 a_p + \frac{1}{2!} (C_2^0 p a_{p-1} + C_2^1 a_p)$$

and

$$\int_0^1 (x^2 + x^3 + \dots x^{n-1}) \lg^2 dx = 2 \left(\frac{C_3^0}{3!} + \frac{C_4^1}{4!} + \dots \frac{C_n^{n-3}}{n!} \right)$$

$$+ \left(\frac{C_3^2}{3!} + \frac{C_4^3}{4!} + \dots \frac{C_n^{n-1}}{n!} \right) a_1$$

thus

$$\int_0^1 x^n \lg^2 dx = \frac{3!}{n+1!} C_{n+1}^{n-3} + \frac{3}{n+1!} C_{n+1}^{n-1} a_1$$

omitting $a_1 = 0$.

In the same way we find

$$\int_0^1 x^n \lg^4 dx = \frac{4!}{n+1!} C_{n+1}^{n-4} + \frac{4!}{2!n+1!} C_{n+1}^{n-2} a_2 + \frac{4!}{4!n+1!} C_{n+1}^n a_4$$

$$\int_0^1 x^n \lg^5 dx = \frac{5!}{n+1!} C_{n+1}^{n-5} + \frac{5!}{2!n+1!} C_{n+1}^{n-3} a_3 + \frac{5!}{4!n+1!} C_{n+1}^{n-1} a_4$$

and by induction

$$\frac{n+1!}{p!} \int_0^1 x^n \lg^p dx = C_{n+1}^{n-p} + \frac{1}{2!} C_{n+1}^{n-p+2} a_2 + \frac{1}{4!} C_{n+1}^{n-p+4} a_4 + \dots \quad (13)$$

where the last term is $\frac{1}{p!} C_{n+1}^n a_p$ if p is even, and $\frac{1}{p-1!} C_{n+1}^{n-1} a_{p-1}$ when p is odd.

If we substitute this result in (10) remarking that

$$C_{n+1}^r + (n+1) C_{n+1}^{r-1} = C_{n+2}^r$$

we easily find that this equation is satisfied, which proves that (13) is true generally.

9. The numbers of STIRLING of the second kind \mathfrak{S}_{n+1}^ν , which are determined by the expansion

$$\frac{1}{x(x+1) \dots (x+n)} = \frac{\mathfrak{S}_{n+1}^0}{x^{n+1}} - \frac{\mathfrak{S}_{n+1}^1}{x^{n+2}} + \frac{\mathfrak{S}_{n+1}^2}{x^{n+3}} - \dots$$

may also be written in the form of definite integrals.

Starting from the higher difference of a power of the variable x

$$\Delta^n x^\nu = \sum_{s=0}^n (-1)^s \binom{n}{s} (x+n-s)^\nu$$

and integrating both members between the limits 0 and 1, we get

$$\begin{aligned} \int_0^1 \Delta^n x^\nu dx &= \frac{1}{p+1} \sum_{s=0}^n (-1)^s \binom{n}{s} \left[(n+1-s)^{p+1} - (n-s)^{p+1} \right] \\ &= \frac{1}{p+1} \sum_{s=0}^{n+1} (-1)^s \binom{n+1}{s} (n+1-s)^{p+1}. \end{aligned}$$

Comparing this result with the known formula

$$\mathfrak{S}_{n+2}^{p-n} = \frac{1}{n+1!} \sum_{s=0}^{n+1} (-1)^s \binom{n+1}{s} (n+1-s)^{p+1}$$

we obtain

$$\mathfrak{S}_{n+2}^{p-n} = \frac{p+1}{n+1!} \int_0^1 \Delta^n x^p dx.$$

Now $\Delta^n x^p$ has been expressed in the form of a definite integral by LAPLACE (Oeuvres 7 p. 518) in the following way.

By partial integration

$$\int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^{p+1}} = \frac{1}{ip} \left[\left(\frac{e^{-ixs}}{(1-is)^p} \right) + ix \int_{-\infty}^{\infty} \frac{e^{-ixs}}{(1-is)^p} ds \right]$$

or, because

$$\text{mod. } \left| \frac{e^{-ixs}}{(1-is)^\nu} \right| = \frac{1}{(1+s^2)^{\frac{\nu}{2}}}$$

$$\int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^{\nu+1}} = \frac{x}{p} \int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^p},$$

Thus also

$$\int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^p} = \frac{x}{p-1} \int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^{p-1}}$$

$$\int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^2} = \frac{x}{1} \int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{1-is}$$

and by multiplying all these equations

$$\int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{(1-is)^{p+1}} = \frac{x^p}{p!} \int_{-\infty}^{\infty} \frac{e^{-ixs} ds}{1-is}$$

Now the last integral has the value

$$\int_{-\infty}^{\infty} \frac{(\cos xs - i \sin xs)(1+is)}{1+s^2} ds = 2 \int_{-\infty}^{\infty} \frac{\cos xs + s \sin xs}{1+s^2} ds = 2\pi e^{-x}$$

therefore

$$\int_{-\infty}^{\infty} \frac{e^{x(1-is)}}{(1-is)^{p+1}} ds = 2\pi \frac{x^p}{p!}$$

and

$$x^p = \frac{p!}{2\pi} \int_{-\infty}^{\infty} \frac{e^{x(1-is)} ds}{(1-is)^{p+1}}$$

Hence

$$\Delta^n x^p dx = \frac{p!}{2\pi} \int_{-\infty}^{\infty} \frac{\Delta^n e^{x(1-is)}}{(1-is)^{p+1}} ds = \frac{p!}{2\pi} \int_{-\infty}^{\infty} \frac{e^{x(1-is)} [e^{1-is} - 1]^n ds}{(1-is)^{p+1}}$$

and, integrating between 0 and 1

$$\int_0^1 \Delta^n x^p dx = \frac{p!}{2\pi} \int_{-\infty}^{\infty} \frac{(e^{1-is} - 1)^{n+1}}{(1-is)^{p+2}} ds$$

thus

$$\mathfrak{E}_{n+2}^{p-n} = \frac{p+1!}{2\pi (n+1)!} \int_{-\infty}^{\infty} \frac{(e^{1-is} - 1)^{n+1}}{(1-is)^{p+2}} ds$$

or

$$\mathfrak{E}_{n+1}^p = \frac{p+n!}{2\pi \cdot n!} \int_{-\infty}^{\infty} \frac{(e^{1-is} - 1)^n ds}{(1-is)^{p+n+1}}$$

Finally we remark that the function

$$\mathfrak{E}_{n+1}^p(\alpha) = \frac{1}{n!} \sum_{s=0}^n (-1)^s \binom{n}{s} (\alpha + n-s)^{n+p}$$

may also be expressed by the definite integral

$$\frac{p+n!}{2\pi \cdot n!} \int_{-\infty}^{\infty} \frac{(e^{1-is} - 1)^n e^{(1-is)\alpha}}{(1-is)^{p+n+1}} ds.$$

Physiology. — "*Further researches on periodic nuclear division*".

By Mistress C. E. DROOGLEEVER FORTUYN—VAN LEYDEN. (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of February 23, 1924).

Having noticed in 1916¹⁾ a certain periodicity in the nuclear division of some tissues of the cat I meant to have to continue the investigation to see 1° whether also other tissues of the same animal would show the phenomenon and 2° whether also other animals would do so. The answer on the first question was affirmative. The second investigation had no particular result.

As before, six new-born cats formed the material. They were killed on the third day of their life at 2½, 6½ and 10½ p. m. and a. m. The following organs have been fixed in the mixture of Carnoy immediately after death: Thymus, lymph-gland, spleen and bone-marrow. They were chosen because they are all related with the formation of the blood. The organs were cut into serial sections and the sections were stained with iron-haematoxylin-eosin. The nuclear divisions were counted in the same way as before (1916). The acquired figures could be composed into the following table. Here the figures are indicating the percentage of nuclear divisions in the total number of counted nuclei.

| Time | Thymus | Lymph-gland | Spleen | Bone-marrow |
|---------|---------------|---------------|---------------|---------------|
| 2½ a.m. | 2.630 ± 0.204 | 1.623 ± 0.161 | 0.421 ± 0.082 | 0.262 ± 0.065 |
| 6½ " | 0.748 ± 0.111 | 0.893 ± 0.128 | 0.416 ± 0.083 | 0.263 ± 0.065 |
| 10½ " | 0.700 ± 0.106 | 0.532 ± 0.093 | 0.131 ± 0.046 | 0.177 ± 0.053 |
| 2½ p.m. | 2.236 ± 0.188 | 0.600 ± 0.098 | 1.024 ± 0.125 | 0.00 |
| 6½ " | 1.439 ± 0.149 | 1.193 ± 0.041 | 0.179 ± 0.054 | 0.048 ± 0.027 |
| 10½ " | 1.722 ± 0.165 | 2.841 ± 0.214 | 0.411 ± 0.082 | 0.326 ± 0.072 |

¹⁾ Some Observations on Periodic Nuclear Division in the Cat, Proceedings Kon. Akad. v. Wetensch. te Amsterdam, Vol. XIX.

As before, we see, with the exception of the thymus and the spleen at $2\frac{1}{2}$ p. m., a certain periodicity viz. a maximum of nuclear divisions at night and early in the morning ($10\frac{1}{2}$ p. m. and $2\frac{1}{2}$ a. m.) and a minimum of karyokineses at noon ($10\frac{1}{2}$ a. m. and $2\frac{1}{2}$ p. m.). During the intermediate hours ($6\frac{1}{2}$ a. m. and $6\frac{1}{2}$ p. m.) again a gradual transition could be observed.

In connection with our previous observations the phenomenon is too obvious to be ascribed merely to chance. The cause of the two exceptions could not be found. Both these exceptions, thymus and spleen at $2\frac{1}{2}$ p. m., occurred in a single specimen. The 5 other kittens behaved themselves as could be expected after my first examination. One could guess a lack of health in the deviating animal, but nothing is known in this respect.

Besides the cat also organs of tadpoles and of young chickens were studied in the same way, but without positive result. The following table of the tadpole f.i. shows no periodicity.

| Time | Fore-brain | Thalamus | Rhombencephalon | Fore-leg |
|-------------------|------------|----------|-----------------|----------|
| 3 a.m. | 0.504 | 0.692 | 0.463 | 1.051 |
| 7 " | 0.499 | 0.706 | 0.283 | 1.272 |
| $11\frac{1}{2}$ " | 0.262 | 0.058 | 0.176 | 0.210 |
| 3 p.m. | 0.967 | 0.793 | 1.126 | 1.618 |
| 7 " | 0.557 | 0.662 | 0.411 | 0.552 |
| $10\frac{3}{4}$ " | 0.874 | 0.924 | 0.697 | 2.692 |

I wish to point out that one has to mind the hour of death of the animal when one studies the formation of the blood in mammals.

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Zoology. — “*The significance of the interstitium testis in fishes*”.

By Dr. G. J. VAN OORDT. (Communicated by Prof. J. BOEKE).

(Communicated at the meeting of February 23, 1924).

My investigations concerning the changes occurring in the testis of the ten-spined Stickleback at the appearance of the secondary sex-characters, gave rise to the opinion (VAN OORDT 1923, 1924*a*, 1924*b*) that in *Gasterosteus* the sex-hormones are not formed by the interstitial cells. It is most probable that to these cells, which are periodically found in large numbers in the testis, only a trophic function must be attributed.

In spring, when the secondary sex-characters of the Stickleback develop, the interstitial cells (cells of LEYDIG) strongly increase in number. It was especially this observation which caused COURRIER (1922) to hold the opinion that the sex-hormones are exclusively secreted by the interstitial cells. It appeared to me, however, that ♂♂ are also found, the testes of which contain numerous interstitial cells, but in which the sex-characters are not developed at all. So the presence of numerous cells of LEYDIG need not always coincide with the development of the secondary sex-characters.

In all cases observed by me, in which the interstitium testis was enlarged and in which the number of interstitial cells had strongly increased — so as well in the ♂♂ just mentioned, as in the ♂♂, in which the sex-characters had developed — the spermatogenesis had come to an end. By this fact it was stated that a relation may exist between the spermatogenesis and the number of interstitial cells.

As after the formation of the spermatozoa a period of spermatogenous rest occurs in the testis and as the interstitial cells always increase in number at the beginning of this period, I think I can formulate the relation between spermatogenesis and these cells as follows. I am of opinion that the nutritive substances, conducted to the testis during spermatogenesis and then regularly consumed by the spermatogenous cells, are still conducted to the testis after the spermatogenesis has come to an end, but that they are now deposited in the strongly increasing interstitial cells, because they are no longer consumed. Here these substances remain till they are absorbed in the beginning of the following spermatogenous period (in early autumn in *Gasterosteus*).

I have continued my investigations, concerning the changes taking place in the testis at the appearance of the secondary sex-characters in a second species of fishes viz. *Xiphophorus Helleri* Heckel, a fish imported from Mexico in 1909, of which the ♂♂ show very distinct sex-characters. These, however, do not develop periodically as is the case in *Gasterosteus*, but are permanently present. The investigations concerning the changes in the testis of the young males, in which the secondary sex-characters are forming, have by no means come to an end; so I can only communicate my observations, concerning the interstitium testis of this species.

Xiphophorus Helleri received this name, because in the ♂ the ventral part of the caudal fin is extremely elongated. Like so many fishes, kept in warm water aquaria at present, this species also belongs to the family of the viviparous *Cyprinodontidae*. In the male the anal fin has been transformed into an intromittent organ or gonopodium, which conducts the sperma into the oviduct of the female. Besides the caudal fin, so markedly elongated, and the gonopod, the ♂ possesses still another distinct sex-character: the pelvic fins are longer and narrower than those of the ♀. Finally the body-form of the ♂ is slenderer than that of the ♀. A good drawing of ♂ and ♀ can be found in BREHM's Tierleben (vol. III, p. 319).

Originally the testes are paired (ESSENBERG 1923), but they soon fuse to form a more or less compact organ. The structure of the male gonad is in short as follows. The numerous testis-tubules begin blindly at the periphery of the gland; they are narrow and consist of a large number of spermatocysts, situated one behind the other. Just as is the case in *Gasterosteus* in each spermatocyst numerous spermatozoa or spermatogenous cells are found, which are all in the same stage of division. The oldest spermatogenous cells are also situated at the periphery, the younger ones more to the centre of the gonad. In each spermatocyst one spermatophore is finally formed. The periphery of these spherical bodies consists of the spermatozoa-heads, closely pressed together, while the tails belonging to them are twisted and directed towards the centre of the spermatophore. The testis-tubules open into numerous efferent ducts, which are connected with the ductus deferens.

The testis of the young male, in which the gonopod has just been formed and the caudal fin of which begins to elongate, also shows the same structure. However, in these animals no spermatophores or only very few have been formed and only a few spermatocysts with spermatids or spermatozoa are present. In the adult male the spermatophores are found in large numbers.

The interstitium testis of a male, in which the secondary sex-characters develop, is very narrow: only here and there between the spermatocysts a few connective tissue-nuclei and very narrow bloodvessels are found. Interstitial cells are only met with in a few places in very small numbers. The interstitium of the adult male is also very narrow, especially at the periphery of the testis between the spermatocysts with spermatogenous cells. More to the centre the interstitial tissue is somewhat wider and here, especially at the place, where the spermatocysts with spermatozoa and spermatophores are situated, there are a few small groups of interstitial cells. The total number of cells of LEYDIG is very small, however.

If the sex-hormones were formed in the interstitium, we would expect a wide interstitium with numerous interstitial cells in young males, in which the secondary sex-characters appear and in adult males, in which these characters are completely developed. We saw that this was not the case, however. Therefore, as is the case in *Gasterosteus*, a relation does not exist between the secondary sex-characters and the interstitial cells in *Xiphophorus*. The sex-hormones of these fishes are not formed in the interstitial cells.

CHAMPY (1923), who communicates in a short article the results of his investigations, concerning the presence of interstitial cells in Fish-species with secondary sex-characters, did not find interstitial cells in the testis of *Xiphophorus Helligeri*. Neither do ESSENBERG's figures of testis-sections of this species show interstitial cells.

What is the cause of the testis of *Gasterosteus* possessing numerous interstitial cells during a certain time of the year — on purpose I only mention the two species examined — whereas the male gonad of *Xiphophorus* shows them in such very small numbers? To answer this question we must remember the fact that the males of *Gasterosteus* are only in heat once a year i. e. in spring. During this time the testis is in the period of spermatogenous rest, above mentioned. It is most probable that then the substances, which are consumed by the spermatogenous cells during spermatogenesis, are deposited in the interstitium and that the number of interstitial cells strongly increases. The ♂ of *Xiphophorus*, however, can fertilize all the year round, the ♀ also gives birth to young all the year round¹⁾. Spermatophores are constantly formed, a spermatogenous period of rest

¹⁾ Both phenomena are not necessarily related. One fertilization viz. suffices for the development of several generations of young; cf. the investigations of GERSCHLER (1914) and of Ö. WINGE (1922).

does not exist. The substances conducted to the testis, are directly consumed and so they are not deposited in the interstitial cells during a part of the year. Between those parts of the testis-tubules, where spermatogenous cells are found, no interstitial cells are met with; only there where the spermatocysts contain spermatozoa or spermatophores and the nutritive substances are consequently not consumed for some time, a few very small groups of cells of LEYDIG are found.

It is my opinion that the marked difference in structure of the testis and especially of the interstitium testis of *Gasterosteus* and *Xiphophorus* can only be explained in this way. We shall have to await whether the results of investigations in other (tropical) species of fishes, which do not have a fixed time of heat and of which the ♂♂ can also fertilize all the year round, will confirm the working-hypothesis here given.

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Physics. — “*Dispersion of Light by Irregular Refraction and by Molecular Scattering*”. By Dr. J. SPIJKERBOER. (Communicated by Prof. W. H. JULIUS).

(Communicated at the meeting of December 29, 1923).

1. *Introduction.* In the explanation of the general distribution of light over the sun's disc as well as in the inquiry into the distribution of intensity in the solar spectrum the scattering by irregular refraction and the molecular scattering must be taken into account.

If molecular scattering can to a great extent be the cause through which the diminution of intensity ¹⁾ from centre towards limb of the sun's disc, also for different wave-lengths, is as it is observed, it is the irregular refraction which, as Professor JULIUS has shown, can also play a part in this, and can also account for the origin of the sharp solar limb.²⁾

As both the irregular radial curvature and the molecular scattering become very considerable for light from the immediate neighbourhood of absorption lines³⁾, it must be assumed that the FRAUNHOFER lines are absorption lines which are enveloped by dispersion bands.

Both in the study of the “structure of the solar radiation” ⁴⁾ and in that of the “relation between the broadening and the mutual influence of dispersion lines in the spectrum of the sun's limb” ⁵⁾ we are confronted by the question of the greater or smaller influence of the molecular scattering or of the scattering by refraction. So far the influence of these two causes of scattering on each other has not been taken into account.

The purpose of this paper is to examine how we must imagine this mutual influence to be, and what conclusions can be derived from it. It seems to me that we are not justified in leaving these conclusions out of consideration.

2. *Scattering through irregular refraction.* In a paper on “Regular Consequences of Irregular Refraction in the Sun” ⁶⁾ Professor JULIUS

¹⁾ J. SPIJKERBOER, *Verstrooiing van licht en intensiteitsverdeling over de zonneschijf*. Proefschrift. Utrecht 1917; Arch. néerl., IIIA, V, 1, 1918.

²⁾ W. H. JULIUS, *Astroph. Journ.*, **38**, 129, 1913.

³⁾ W. H. JULIUS, *These Proc.*, Vol. XII, p. 266, 1909; Vol. XIII¹, p. 2, 1910; Vol. XIII^{II}, p. 881, 1911; *Handwörterbuch der Naturwissenschaften*, VII, 832.

⁴⁾ P. H. VAN CITTERT, *These Proc.*, Vol. XXII, p. 73, 1919.

⁵⁾ W. H. JULIUS and M. MINNAERT, *These Proc.*, Vol. XXVI, p. 329, 1923.

⁶⁾ W. H. JULIUS, *These Proc.*, Vol. XII, p. 266, 1909.

decided the question in 1909 what must be the influence of anomalous dispersion on the width of the so-called absorption lines in the sun's spectrum, if throughout the sun's atmosphere there are gradients of density which in many places are supposed to be of the same order of magnitude as in the spots, but which repeatedly reverse their signs.

If in the sun's atmosphere there is a spherical region C (fig. 1),

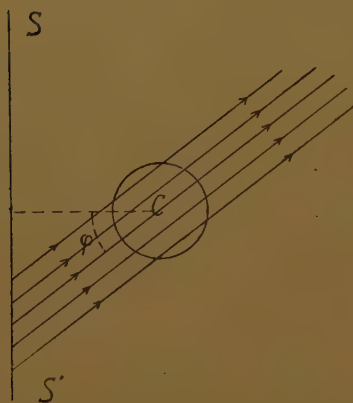


Fig. 1.

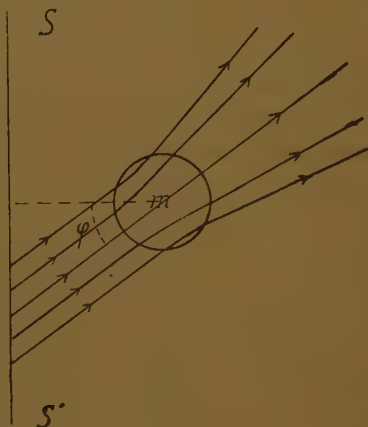


Fig. 2.

inside which the density does not deviate from that of the surroundings, the radiation, which leaves the surface SS' ¹⁾ at an angle φ with the normal, will permeate this region C without change of direction.

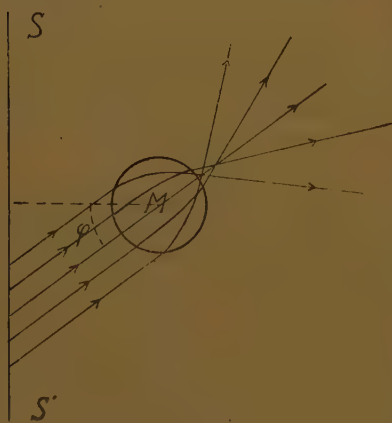


Fig. 3.

In a region with a density gradient such that the density in m (fig. 2) is a minimum, the incident beam is broadened like a plume; the same thing holds if there exists a gradient of density in this spherical region with a maximum of density in M (fig. 3) ²⁾. This plume-like broadening will be dependent in a great degree on the way in which the density

¹⁾ We may imagine the surface SS' lying so deep within the sun's atmosphere that the radiation follows the cosine law there; we may also assume that the surface SS' is imagined so that outside it the radiation is so small that it is a negligible fraction of the total energy emitted; we further call the surface SS' the surface of the nucleus.

²⁾ Compare also a paper by L. S. ORNSTEIN and F. ZERNIKE, These Proc., Vol. XXI, p. 115, 1917.

varies within the regions m and M ; in different cases the rays of light will present a course entirely different from that represented in fig. 2 and fig. 3, but this broadening, both in the case that there occurs a maximum and in the case that there occurs a minimum of density, will always vary with the refractivity in the atmosphere, and it will, therefore, depend on the density and the refraction-constant. Hence the broadening will become considerable for light of a wave-length differing little from the wave-length of an absorbed vibration, at least if the density of the component that produces the absorption line, is not too small.

Thus if the angle φ becomes greater or if the refractivity is more considerable than in the cases drawn in fig. 2 and fig. 3, part of the incident radiation can, for a definite frequency, return to the surface of the nucleus SS' , and consequently not leave the sun.

By integration round the normal from C on SS' (over 2π) and over φ (from 0 to $\frac{\pi}{2}$) is found the radiation which penetrates the region C , and which would also leave the sun if there was no radial curvature.

If radial curvature is taken into account, part of the incident energy returns from m or M to the surface of the nucleus, and this part is the greater as the refractivity is the more considerable, variations of density being the same.

By considering only the effect of the radial refraction, and by assuming that there are several of these regions m and M in the sun's atmosphere, we must conclude that into the regions lying nearer SS' there can also penetrate radiation which was curved within the regions lying further from the nuclear surface so, that it returned to SS' ; of this energy striking M or m at an angle $\varphi > 90^\circ$ part will recede once more from the sun on account of the refraction in those regions lying nearer. The part of the returned radiation that does leave the sun's atmosphere in this way will, however, be of little importance, at any rate only a small fraction of the intensity which of the radiation was sent back by the first curvature.

3. Molecular scattering. Let us now consider the case that only molecular scattering in the sun's atmosphere is taken into account.

Again SS' be the surface of the nucleus; EE' a boundary layer, outside which no scattering particles are present.

We choose a coordinate x normal to SS' measuring the scattering mass, and for which the increase, as long as the density in the direction perpendicular to SS' does not change, is equal to the

product of the coefficient of scattering s in the region under consideration, and the displacement t normal to SS' . Hence, for a definite point P inside the atmosphere x indicates the sum of the values st between the boundary layer and this point. As the density, and consequently s , will increase towards SS' , a point for which $x = \frac{1}{2}H$, must be imagined to lie nearer A than B , when $x = 0$ is chosen for EE' and $x = H$ for SS' . This supposition has no influence on the further consideration. The place of the layer under consideration can every time be chosen so as to be suitable. For radiation forming an angle i with the

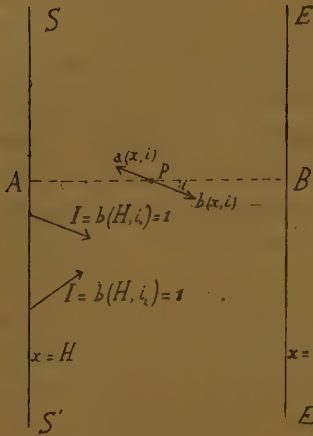


Fig. 4.

normal AB we distinguish radiation b emanating from SS' , and radiation a , returning to SS' . Besides on i , a and b depend on x .

The limiting conditions are: 1. $b(H, i)$ is independent of i and equal to the radiation incident from the surface of the nucleus, which radiation we put 1 (thus finding a and b as fractions of this unit);¹⁾

2. $a(0, i) = 0$.

As solution for a and b is found:

$$a(x, i) = \int_0^x I(\xi) e^{(\xi-x) \sec i} \sec i d\xi, \quad (1)$$

$$b(x, i) = e^{(x-H) \sec i} + \int_x^H I(\xi) e^{(x-\xi) \sec i} \sec i d\xi, \quad (2)$$

in which

$$I(\xi) = \frac{1}{2} \left\{ \int_0^{\frac{\pi}{2}} a(\xi, i) \sin i di + \int_0^{\frac{\pi}{2}} b(\xi, i) \sin i di \right\}.$$

¹⁾ If in connection with what was said in note 1 on page 166, SS' should be imagined so that the radiation outside it should be slight, the first limiting condition would not be fulfilled; though of great importance for the distribution of light over the sun's disc, this question is, however, of minor importance here.

According to an approximation which SCHWARZSCHILD calls "approximation according to SCHUSTER"¹⁾, l is found equal to $\frac{\xi+0,5}{H+1}$.

By insertion into (1) and (2), we get²⁾:

$$a(x, i) = \frac{x + 0,5 - \cos i}{H + 1} + e^{-x \sec i} \frac{\cos i - 0,5}{H + 1}, \quad (1')$$

$$b(x, i) = \frac{x + 0,5 + \cos i}{H + 1} + e^{(x-H) \sec i} \frac{0,5 - \cos i}{H + 1} \quad (2')$$

Where before the value $b(0, i)$ was my chief point of interest, I will now in particular direct the attention to the intensities of radiation a and b for different values of x and i , for some values of H . (Compare the tables on the next page 170).

SCHWARZSCHILD has shown that the approximation obtained in this way, is a very good one. Though the values $b(0, i)$ are more accurately known in the different cases, I have given the approximated values also for them in the above mentioned tables.

The result of the calculations is clearly set forth in the figures 5—7 (p. 171) (fig. 5 for $H=8$; fig. 6 for $H=4$; fig. 7 for $H=1$).

From O the radiation a and b is indicated on the radii vectores from O for the angles for which the cosine possesses the values used in the tables. As the figures show, the angles have been taken with OY as fixed leg.

The full lines apply to the b -radiation, the other lines to the a -radiation.

Besides the intensity of the a -radiation is plotted on the radii vectores from O which give the angles calculated from OY' .

In this way curves are obtained round O which give the intensities of radiation for points as P in fig. 4 in a plane through AB for directions between PA and PB .

On revolution of such a curve round YY' as axis the surface of irradiation of P is formed.

The lines 1, 2, 3 and 4 belong respectively to $x=H$, $x=\frac{1}{2}H$, $x=\frac{1}{4}H$ and $x=0$.

In the X -axis the broken line 1 should come together with the full line 1; the approximation, which was required for all the other lines, but not for the full line 1 is the cause that this does not take place.

¹⁾ Cf. K. SCHWARZSCHILD, Sitzungsberichte Kön. Pr. Ak. d. Wiss., **47**, 1183, 1914 and A. SCHUSTER, Astroph. Journal, **21**, 1, 1905.

²⁾ Compare J. SPIJKERBOER, Dissertatie Utrecht, 45, 1917; Arch. néerl., IIIA V, p. 45, 1918.

TABLE I $H=8$.

| | $\cos i = 1$ | $\cos i = 0.8$ | $\cos i = 0.6$ | $\cos i = 0.4$ | $\cos i = 0.2$ | $\cos i = 0.0$ |
|-----------------------|--------------|----------------|----------------|----------------|----------------|----------------|
| $b(H, i) =$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $a(H, i) =$ | 0.83 | 0.86 | 0.88 | 0.90 | 0.92 | 0.94 |
| $b(\frac{H}{2}, i) =$ | 0.61 | 0.59 | 0.57 | 0.54 | 0.52 | 0.50 |
| $a(\frac{H}{2}, i) =$ | 0.39 | 0.41 | 0.43 | 0.46 | 0.48 | 0.50 |
| $b(\frac{H}{4}, i) =$ | 0.39 | 0.37 | 0.34 | 0.32 | 0.30 | 0.28 |
| $a(\frac{H}{4}, i) =$ | 0.17 | 0.19 | 0.21 | 0.23 | 0.26 | 0.28 |
| $b(0, i) =$ | 0.17 | 0.14 | 0.12 | 0.10 | 0.08 | 0.06 |
| $a(0, i) =$ | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE II $H=4$.

| | $\cos i = 1$ | $\cos i = 0.8$ | $\cos i = 0.6$ | $\cos i = 0.4$ | $\cos i = 0.2$ | $\cos i = 0.0$ |
|-----------------------|--------------|----------------|----------------|----------------|----------------|----------------|
| $b(H, i) =$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $a(H, i) =$ | 0.70 | 0.74 | 0.78 | 0.82 | 0.86 | 0.90 |
| $b(\frac{H}{2}, i) =$ | 0.69 | 0.66 | 0.62 | 0.58 | 0.54 | 0.50 |
| $a(\frac{H}{2}, i) =$ | 0.31 | 0.34 | 0.38 | 0.42 | 0.46 | 0.50 |
| $b(\frac{H}{4}, i) =$ | 0.50 | 0.46 | 0.42 | 0.38 | 0.34 | 0.30 |
| $a(\frac{H}{4}, i) =$ | 0.14 | 0.16 | 0.18 | 0.22 | 0.26 | 0.30 |
| $b(0, i) =$ | 0.30 | 0.26 | 0.22 | 0.18 | 0.14 | 0.10 |
| $a(0, i) =$ | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE III $H=1$.

| | $\cos i = 1$ | $\cos i = 0.8$ | $\cos i = 0.6$ | $\cos i = 0.4$ | $\cos i = 0.2$ | $\cos i = 0.0$ |
|-----------------------|--------------|----------------|----------------|----------------|----------------|----------------|
| $b(H, i) =$ | 1 | 1 | 1 | 1 | 1 | 1 |
| $a(H, i) =$ | 0.34 | 0.39 | 0.46 | 0.55 | 0.65 | 0.75 |
| $b(\frac{H}{2}, i) =$ | 0.85 | 0.82 | 0.78 | 0.71 | 0.61 | 0.50 |
| $a(\frac{H}{2}, i) =$ | 0.15 | 0.18 | 0.22 | 0.29 | 0.39 | 0.50 |
| $b(\frac{H}{4}, i) =$ | 0.76 | 0.72 | 0.66 | 0.58 | 0.48 | 0.38 |
| $a(\frac{H}{4}, i) =$ | 0.07 | 0.08 | 0.11 | 0.15 | 0.23 | 0.38 |
| $b(0, i) =$ | 0.66 | 0.61 | 0.54 | 0.45 | 0.35 | 0.25 |
| $a(0, i) =$ | 0 | 0 | 0 | 0 | 0 | 0 |

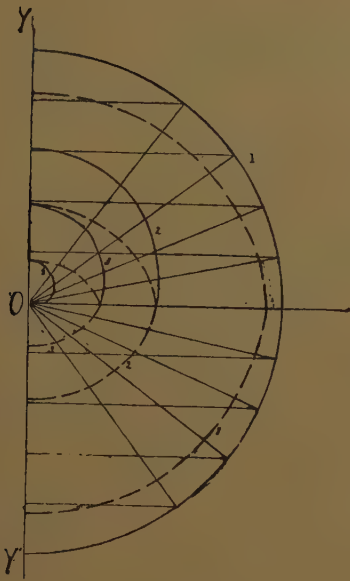


Fig. 5.

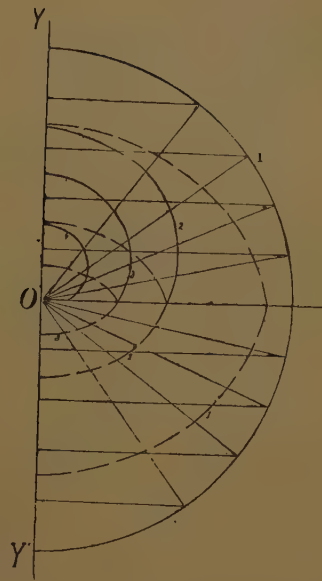


Fig. 6.

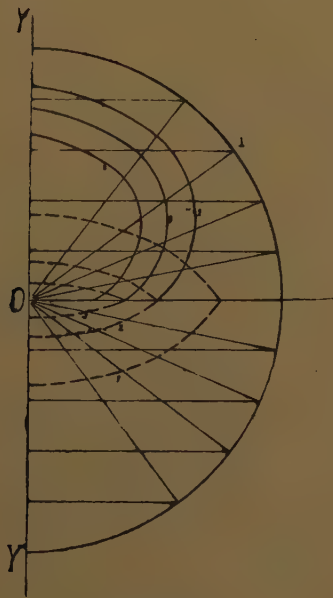


Fig. 7.

Also the molecular scattering causes part of the radiation leaving SS' to return to the surface of the nucleus. This is even an important part for great values of H .

Scattering by refraction and molecular scattering both contribute to an economical consumption of the energy present inside the nuclear surface and radiated to the outside, which is emitted more slowly than would be the case without scattering¹⁾.

4. *An atmosphere with refractional scattering and molecular scattering.* Finally we raise the question what will be the consequences

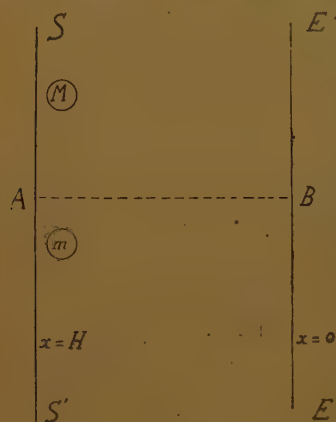


Fig. 8.

of irregular refraction in an atmosphere in which also the molecular scattering is thought of importance. For this purpose we again imagine the scattering atmosphere of § 3, but now with regions inside which the density differs appreciably from that of the surroundings, hence regions M and m . If such a region lies near SS' , where x is about $= H$, we have to bear in mind that besides the b -radiation, also the a -radiation can now be of importance.

It follows from the tables of § 3 that for great values of H the a -radiation does not fall far below the b -radiation, that for smaller values of H the a -radiation may at any rate not be neglected compared with the b -radiation.

If the a -radiation was equal to the b -radiation (also for varying values of i) the scattering by irregular refraction would vanish.

We, therefore, conclude: in an atmosphere with molecular scattering regions where the density varies irregularly and which lie deep in this atmosphere, will be of very small or of less influence

¹⁾ It is not impossible that the same question is of importance in the earth's atmosphere for the explanation of the decrease of the temperature of the layers of air further from the earth; the earth's atmosphere is irradiated with parallel radiation; in consequence of this the a -radiation will be of little importance for the incident radiation; for the energy emitted again by the earth, in which radiation of different direction is to be reckoned with, the a -radiation will be more important; besides, the density near the surface of the earth being greater, the plane $\frac{H}{\lambda}$ will lie near the earth's crust; and moreover H is much greater for radiation of great wave-length; hence the process of retardation will have more influence for the outgoing than for the incident radiation. The meaning is, of course, that this question can also play a part.

on the distribution of light over the different directions, and on the intensity of the emitted radiation according as the scattering atmosphere is deeper or less deep (taking deep in the sense that $s \times t$ is great, i. e. that the scattering mass is great; 8 or more may be called great there).

If a region M or m lies at a depth $x = \frac{1}{2}H$, the importance of the a -radiation with respect to that of the b -radiation, gets into the background. The refractional scattering begins to gain influence. Yet even now the a -radiation remains important for great values of H , and the influence of the refraction remains small; for small values of H the a -radiation is still to be taken into account. Regions M or m lying near EE' , leave the influence of the refractional scattering undiminished.

And in conclusion I will now consider the question whether, if strong irregular refraction is assumed in the outer layers, the part which the molecular scattering will play, may be considered of minor importance. This may certainly not be assumed for radiation which has not its place in the spectrum in the immediate neighbourhood of an absorbed vibration. For the irregular refraction is not anomalous for such radiation, and the irradiation of the regions M or m , which are situated near EE' , is greatly controlled by the molecular scattering; on the regions M or m falls the radiation $b(0, i)$, which in a great degree varies in intensity for other values of i .

But also for radiation that has nearly the same wave-length as an absorption line (absorbent component within M or m), for which the irregular refraction becomes, therefore, anomalous, we cannot say that the molecular scattering does not act its part. For two reasons! For if the same absorbent component is present also in the deeper layers, radiation of a frequency of the immediate neighbourhood of the absorption line will, before it reaches the regions M and m , be already so much weakened in consequence of anomalous molecular scattering that the dispersion band (through molecular scattering) will already be present also in the spectrum of the radiation which must still permeate the regions M and m . And if the regions of irregular refraction arise through the motion of gas masses, it is also possible that in such a region M or m the absorbent component is present in a comparatively great degree, though much less outside it. Then the anomalous molecular scattering would also be considerable in those regions M and m , whereas outside these regions the layer is considered as little scattering.

Bussum, November 1923.

Chemistry. — "*Complex Boric-Acid Compounds and the Optically Active Boron Atom*". By Prof. J. BÖESEKEN and J. MEULENHOF.

(Communicated at the meeting of January 29, 1924).

In a communication in these proceedings on the „valency of boron”¹⁾ some compounds were mentioned of boric acid with pyrocatechine both with aliphatic and aromatic hydroxy acids, which have been described more fully by Mr. P. H. HERMANS²⁾. Their constitution can be brought in symbol in the simplest way by the assumption that the boron atom with *four* valencies was bound to two molecules of the organic poly oxy compound, thus forming a monovalent anion:



Fig. 1.

In order³⁾ to get a closer confirmation of this view a number of new compounds of this type were prepared synthetically, and it was tried to furnish the definitive proof of this constitution by effecting the splitting up into optical antipodes of a derivative, the anion of which cannot coincide with its mirror image.

This is the case with the borosalicylates, where we have to do with the optically-active spirane compound, as can be easily derived from the adjoined symbol (next page).

¹⁾ These Proceedings 26, 97 (1923)

²⁾ These Proceedings 26, 32 (1923).

As regards the first part of this task, besides the potassium salt already described, the following salts were prepared and analysed: ammonium-, aniline-, parachloraniline, dimethylaniline-, and pyri-

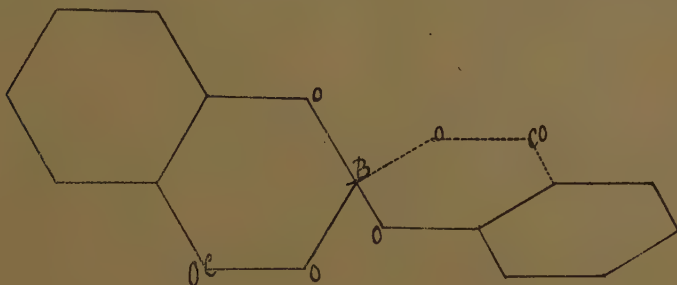


Fig. 2.

dine salt of the dipyrocatechine boric acid; besides by careful heating, the free acid was prepared from the aniline salt; it appeared to be undecomposed volatile.

All these salts have the composition:



and crystallized without crystal water. The ammonium salt was undecomposed volatile; from the aniline salt the acid was obtained which had the concentration $[B(O_2C_6H_4)_2] H$.

Further the aniline and pyridine salts of dipyrrogallol boric acid were prepared; as further salts of this acid did not readily crystallize, no further attempts were made to obtain optical antipodes, which are theoretically possible.

Then the influence on the conductivity of boric acid was determined for the two nitro pyracatechines 1.2.3 and 1.2.4, which was very great: for $\frac{1}{16}$ normal to $\frac{1}{2}$ mol. H_3BO_3 at 25° of 1.2.3 = 1163×10^{-6} Kohlrausch-Holborn-units, for 1.2.4 = 302×10^{-6} .

What is remarkable here is the much stronger action of the nitro-group in the ortho-position, which will very likely be due for the greater part to the more strongly acid character of the nitro pyrocatechine part in the boro-complex. In pyro catechine itself this increase of the conductivity amounted to = 137.2 for the same concentration.

Potassium-, ammonium, and aniline salts of di-(3 nitropyrocatechine) boric acid were prepared and analysed; they crystallized without water of crystallisation; attempts to prepare the free complex acid from the aniline salts by distilling the aniline away, did not succeed, as aniline did not escape until a temperature was reached at which decomposition set in. Also of the isomer 4 nitropyrocatechine-boric

acid the corresponding salts were obtained, which like those of the isomer crystallized without crystal water. The constitution was $[B(O, B, H, NO)_2] \cdot R$.

Though these nitropyrocatechine borates might be used for the splitting up into optical isomers, we have preferred to take boro salicylic acid for this purpose, in view of the lengthy process of preparation of larger quantities of the nitropyrocatechines. Experience had taught us that the complex boro-salts of this acid crystallized exceedingly well; besides the acid itself is accessible in unlimited quantities.

First a number of salts was prepared. In anhydrous condition all of them had the constitution $[B(O, COC_6H_4)_2]R$, in which R represents one equivalent of a base.

The aniline-, ammonium-, potassium-, sodium-, silver salts crystallized without water of crystallisation, the pyridine salt with one molecule. The salts of zinc, copper, cobalt, manganese^{II}, nickel, magnesium, and calcium were very fine, they all crystallized with *ten* molecules of water of crystallisation and are probably isomorphous.

The colour of copper-, cobalt, and manganese salts differed from that of the anhydrous anorganic salts. Copper salt was light *green*, cobalt salt salmon-coloured, manganese salt light *yellow*. This and the fact that heterogeneous metals, as copper and calcium, range themselves with zinc and manganese, makes it probable that the great anion constitutes here the formative part of the salt, and that the water molecules probably from part of this anion.

The strontium-, barium-, and lead salts agree with each other as regards form and the absence of water of crystallisation.

With regard to the splitting up of the boro-salicylic acid in the optically active components, we have succeeded in showing the asymmetry of the anion in the *strychine* salt with certainty.

This was obtained from very diluted aqueous-alcoholic solutions in rodlike crystals or in more felty needles.

In fractionated crystallisation the different fractions appeared to have the same constitution as the salts with organic bases described, only the rotations differed, e.g. $+14^\circ.5$, 0° , $-7^\circ.6$, and $-11^\circ.9$.

By shaking with $CHCl_3$, a preparation $[\alpha]_D = +22^\circ.6$ was obtained from the dextro-rotatory fraction; as salicylic acid-strychnine and the base itself, the latter either in the presence of boric acid or not, are laevo-rotatory or feebly dextro-rotatory ($[\alpha]_D = +2^\circ.5$) in chloroformic solution, the proof of the activity of the anion had been given by this.

This salt, which evidently is more sparingly soluble than the laevo-rotatory isomer, is consequently the *d'l-strychnine-borosalicylate*.

If the solution of this salt in $CHCl_3$ was dried with $CaCl_2$, the rotatory

power diminished, becoming laevo-rotatory after some time, and finally constant at $-13^{\circ}.3$. Inversely a laevo-rotatory fraction was reduced to the same value. That this was the consequence of traces of water, was proved as follows: if the solvent was dried with P_2O_5 , the rotatory power also diminished, but much more slowly. In a check experiment with the same positive-rotatory preparation $[\alpha]_D = +11^{\circ}.2$, hence a mixture with an excess of d'l, one specimen dissolved in $CHCl_3$, dried on $CaCl_2$, another specimen in the same solvent dried on P_2O_5 , the former had reached the final rotation $[\alpha]_D = -13^{\circ}.3$ already after seven days, the latter after three weeks.

We see accordingly that traces of H_2O effect a racemation, which is to be expected here, as the borosalicylic acid salts in H_2O are partially hydrolyzed, and are then, of course, very rapidly racemized. Also with brucine similar phenomena were observed; fuller information will be given in the thesis for the doctorate of Mr. MEULENHOF.

Delft, January 1924.

Chemistry. — "*The Configuration of the Hydrobenzoins in Connection with the Situation of the Hydroxyl-Groups in Space.*"

By Prof. J. BÖESEKEN and P. H. HERMANS.

(Communicated at the meeting of January 29, 1924).

In the investigation on the action of boric acid on α -hydroxy-acids it has appeared that the position of the hydroxylgroup of the carboxyl group with regard to the alcoholic hydroxyl group is a function of the groups of the α -C-atom in this sense that the substitution of alkyl- or phenyl groups for H-atoms renders the two OH-groups the more easily accessible to boric acid. It appears from observations by WILLSTÄTTER¹⁾ that this may also be assumed for the formation of cyclic acetone-compounds.

As we have concluded from observations on α -ketonic acids and α -diketones that they are more or less hydrated in aqueous solution, a small variation of position of the groups of the α -C-atom with regard to the hydrated carboxyl group can bring about a considerable modification in their behaviour towards boric acid and acetone²⁾.

Increase of molecular conductivity 0.5 m H_3BO_3 .

| Acid. 1. | $\Delta \times 10^{-2}$ mol _{15°} | $K_{25^\circ} \times 10^4$ 3. | Acid. 1. | $\Delta \times 10^{-2}$ mol _{15°} | $K_{25^\circ} \times 10^4$ 3. |
|-----------------------------|---|----------------------------------|----------------------------|---|----------------------------------|
| $H_2C(OH)COOH$ | 50—100 | 1.54 | $C_6H_5CH(OH)COOH$ | 372 | 4.3 |
| $CH_3CH(OH)COOH$ | 298 | 1.38 | $C_6H_5CH_2CH(OH)COOH$ | 797 | 9.0 |
| $CH_3CH_2CH(OH)COOH$ | 888 | 1.07 | $C_6H_4CH_2CH(OH)COOH$ | 580 | 11.8 |
| $CH_3CH_2CH_2CH(OH)COOH$ | 1144 | 1.24 | $C_6H_2(CH_3)_3CH(OH)COOH$ | 316 | 2.13 |
| $C_6H_5CH_2CH(OH)COOH$ | 334 | 1.89 | $COOHCH_2CH(OH)COOH$ | 340 | 3.78 |
| $C_6H_{13}CH(OH)COOH$ | 493 | 1.55 | $COOHCH_2CH_2CH(OH)COOH$ | 777 | 8.5 |
| $\langle \rangle C(OH)COOH$ | 1041 | 0.54 | Racemic acid | 733 | 10.2 |
| $CH_2OHCH(OH)COOH$ | 338 | 2.8 | Meso tartaric acid | 659 | 6.8 |

¹⁾ Berichte **56**, 2107 (1923).

²⁾ Recueil **40**, 580 (1921).

As regards the influence of the hydroxy-acids on the conductivity of boric acid, the above table (column 2) sets forth the above mentioned modifications very clearly.

We have also inserted the dissociation constants of the acids (column 3) to bring out that the acidifying amount of the acid residue can only be of subordinate significance.

In order to study the influence of different groups it is, therefore better to start from the ethylene glycol, and substitute in this definite groups for the hydrogen atoms. It has, however, appeared that the great majority of the glycols do not exert a positive action on the conductivity of boric acid; we have explained this by the assumption that the hydroxyl groups repel each other, in consequence of which they get an unfavourable position, i.e. on either side of the axis connecting the two hydroxyl-bearing C-atoms, which is the cause that they will not easily form cyclic compounds, resp. these compounds will be very greatly hydrolysed in aqueous solutions.

It is, however, self-evident that some particular groups at these C-atoms can exercise an action on each other and on the OH-groups, through which the state of equilibrium of the molecule can be modified in such a way that the OH-groups are again directed towards each other.

In the course of our researches we have already met with such cases in the esters and the amides of tartaric acids¹⁾. When it is assumed for the first that the repulsive action of the carboxalkyl-groups on each other is much greater than of the OH-groups inter se, the ester of the active acid will sooner exert a positive action than that of the anti-acid, which has been found. This is likewise the case with the amides; here, however, a not inconsiderable increase of the conductivity has been found in the anti-amides, so that there must also operate attractive actions, which for the present do not admit of a simple interpretation.

In these glycols there always remains a possibility that the acidifying action of the groups in the glycol — even though this glycol itself should remain neutral — plays a part in the complex boric acid compound, just as the hydroxyl group, which is not acid in itself, does in the α -hydroxy-acids, so that e. g. nitromethyl-2-propanediol 1.3 may not be compared with propane diol 1.3 and α -monochlor hydrine not with propane diol 1.2.

If however in glycols with *equal* groups, as in the derivatives of tartaric acids, a difference in action is found, this may undoubtedly,

¹⁾ Verslag van de vergad. der Akademie, 29, 272 and 562 (1920).

at least for the greater part, be ascribed to a difference of position of the groups in space, and this especially when this difference in action runs parallel with the behaviour of these substances towards acetone.

In both cases we have, indeed, to do with an action which rests on the formation of an analogous compound:



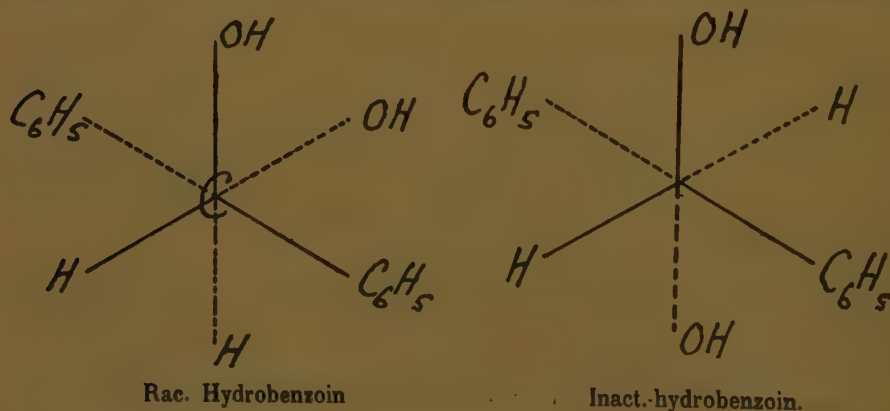
If a greater increase of the conductivity is combined with a higher constant of the acetone equilibrium, we may say with certainty that this must be attributed to a more favourable situation of the hydroxyl groups.

In inactive hydrobenzoin and rac-hydrobenzoin we have found what follows:

| Substance | K-acetone equilibrium at 25°. | Increase of the conductivity of a $\frac{1}{2}$ m. H_3BO_3 . |
|---------------------|----------------------------------|---|
| inact.-hydrobenzoin | 0.44 | — 1 |
| rac- " | 8.56 | + 10 |

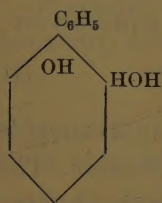
(The solvent was a mixture of 1 mol. acetone and 0.98 mol. water.)

The measurements of the conductivity took place with $\frac{1}{7}$ mol. sol. in 72 % alcohol, on account of the small solubility of hydrobenzoin in water. This result is in perfect harmony with that of the tartaric acid esters, and we may draw the conclusion from this that the mutual repulsion of the phenyl groups exceeds that of the hydroxyl groups, in consequence of which the hydroxyl groups in racemic hydrobenzoin are very strongly inclined towards each other:



A repulsive action between phenyl- and hydroxyl group, if present, would have to increase the difference here still, as in racemic hydrobenzoin it forces the hydroxyl groups towards each other, but does not manifest itself in inactive hydrobenzoin through intermolecular compensation. The very high acetone constant of the rac. hydrobenzoin points indeed in this direction.

This consideration bears a somewhat speculative character, but it is supported by an observation made by Mr. MAAN in this laboratory which can only be accounted for by the assumption of a repulsive action between phenyl and hydroxyl group.¹⁾



It was found in the preparation of the phenyl 1 cyclohexanediol 1.2 that under the influence of traces of acid at about 100° the transdiol changed into a mixture of isomers consisting for the greater part of cis-diol. It follows from this that* the phenyl group at 1 presses the OH-group at 2 to the side of the plane where the other OH-group lies, whereas the hydroxyl groups repulse each other in other cases.

Though in virtue of the results reached so far we are justified in pursuing the course we have followed, we must bear in mind that a perfectly accurate knowledge of the arrangement of the groups in space will never be reached by this simple way, because there are too many unknown factors in the value of the conductivity, and (though in a smaller degree) in that of the equilibrium constant of the acetone equilibrium. Mr. P. H. HERMANS will set this forth in full in a thesis for the doctorate, which will shortly be published. A few points may, however, be pointed out here.

In earlier treatises²⁾ the significance was pointed out of the geometrical studies of SACHSE³⁾ on the stability of ring-systems in connection with the occurrence or absence of a positive influence of cyclic cis 1.2 diols on the conductivity of boric acid. When it is assumed that the affinity directions between the C-atoms always form angles of $\pm 109^{\circ}$, the atoms of saturated rings with five or fewer atoms will lie in one plane, but not those of greater ring-systems. If the complex boric acid compound possesses a five-ring, they will easily form only when the two OH-groups lie in the same plane with the C-atoms to which they are bound, the chance

¹⁾ Berichte 56, 2411 (1923).

²⁾ Cf. inter alia Recueil 40, 553 (1921).

³⁾ B 23, 1363 (1890) Zeitsch. f. physik. Chem. 10, 228 (1890).

is greatest then, *apart from other factors that determine the formation of a compound.*

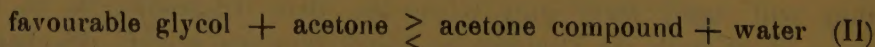
That these other factors can sometimes be very important may perhaps appear most clearly in the cyclic acetone compounds, which according to their analysis and properties certainly possess a five-ring. The orthodihydroxy derivatives of benzene form no acetone compound, though we know almost with certainty that the two OH-groups have a favourable situation in the above-mentioned sense, and therefore very readily form five-rings with other molecules.

If we confine ourselves to this simpler case of the formation of the acetone compound, we have first to consider the equilibrium:

$$\text{favourable molecules} \geq \text{unfavourable molecules} \quad (\text{I}),$$

in which it is assumed that from time to time the unfavourable molecules may pass into a favourable position through torsion. The state of equilibrium of arbitrary molecules will in general be unfavourable; the fewer molecules are changed into favourable ones in the time unit, the smaller will be the chance that there are formed acetone compounds. This number depends, accordingly, on the velocity with which the parts of the molecule with respect to each other move round the common axis of the two vicinal C-atoms. Besides on temperature and medium, this velocity depends on the nature of the groups at the C-atoms. It further depends on the distance between the favourable position and the state of equilibrium — and it is exactly this factor that we wish to know — because the smaller this distance is the more this favourable position will be passed by the molecules that tend towards equilibrium. As in this process of equilibrium this latter factor experiences an influence from the former, the nature of the groups, comparable values for this equilibrium, resp. of the constant, can only be expected in glycols with analogous, and by preference with equal groups, hence in stereo-isomers.

This is the more cogent when it is considered that the constant of this equilibrium is not directly measurable. For the favourable molecules will certainly not *all* react, though they have all the chance to do so. This is determined by the reaction:



which equilibrium will now again be strongly dependent on the nature of the groups in the glycol. Only analogous groups guarantee comparable values for the constants found, and in equal groups, as in the hydrobenzoin, we may even assume these constants to be

about equal, because the nature of the groups is the same, and only their mutual distances apart (e.g. of the phenyl groups) will probably still have some influence.

If the number of favourable molecules with regard to the number of unfavourable ones is assumed to be very small, the constant of the first equilibrium becomes $K_1 = \frac{C_{\text{favourable glycol}}}{C_{\text{glycol}}}$, whereas in the second

$$K_2 = \frac{C_{\text{acetone compound}} \cdot C_{\text{H}_2\text{O}}}{C_{\text{favourable glycol}} \cdot C_{\text{acetone}}}$$

Working in an excess of aqueous acetone, $C_{\text{H}_2\text{O}} : C_{\text{acetone}}$ remains constant, and we get:

$$K_1 \cdot K_2 = \frac{C_{\text{acetone comp.}}}{C_{\text{glycol}}}$$

If, therefore, K_2 is taken equal for the two hydrobenzoin, a relative measure for the ratio of the glycol molecules situated favourably with respect to the total number, will be found in the ratio of the acetone compound to the glycol.

Mr. HERMANS found it at $25^\circ = 8.56$ for the racemic hydrobenzoin, and 0.440 for the intra-molecular inactive hydrobenzoin. The values were for $50^\circ = 4.29$ and 0.266 . This means that the hydroxyl groups lie very much closer together in the first than in the second. At higher temperature this ratio becomes somewhat less favourable ($19.5 : 16.1$).

As we explained above this was to be expected if a strong repulsion of the phenyl groups inter se, and by the side of this possibly a repulsion of phenyl- and hydroxyl groups, was assumed.

The matter is more complicated in the measurements of the conductivity of boric acid, because here the influence of the acid residue on the conductivity and the less simple constitution of the acid boric-acid complexes, as has been found by Mr. HERMANS¹⁾, have a disturbing action as two new factors, so that only in analogous glycols a comparison of the values is possible and a parallelism between these values and these of the acetone equilibrium constants is to be expected. For the rest I refer for further particulars to Mr. HERMANS' study.

¹⁾ These Proc. 26, 32 (1922).

